

$$\beta = \phi_{C_0} + \frac{D_A}{D_C} \phi_{A_0} + \frac{D_E}{D_C} \phi_{E_0}$$

$$\delta = \frac{K_A P_0}{1+K_A P_0} \left( \frac{K_E}{K_A} - \frac{K_C}{K_A} \frac{D_E}{D_C} - \frac{K_D}{K_A} \frac{D_E}{D_D} \right)$$

with boundary conditions:

at  $\eta = 0$ ;  $\phi_A = \phi_{A_0}$  and  $\phi_E = \phi_{E_0}$  and at  $\eta = 1$ ;  $\frac{d\phi_A}{d\eta} = \frac{d\phi_E}{d\eta} = 0$

Realizing that the overall reaction rate within the pore equals the rate of mass transfer across the pore mouth, the rates of reactions of A and E will respectively be proportional to

$$D_A \left. \frac{d\phi_A}{d\eta} \right|_{\eta=0} \quad \text{and} \quad D_E \left. \frac{d\phi_E}{d\eta} \right|_{\eta=0}$$

and, therefore, selectivity with diffusion effects can be expressed

$$S_D = \frac{D_A \left. \frac{d\phi_A}{d\eta} \right|_{\eta=0}}{D_E \left. \frac{d\phi_E}{d\eta} \right|_{\eta=0}}$$

The rate of reaction without diffusion effect can be obtained from equation (2) and the selectivity without diffusion can be simplified to

$$S_0 = \frac{r_A}{r_E} = \frac{k_1 K_A (\phi_{A_0} - \frac{\phi_{E_0} \phi_{C_0}}{K_1})}{k_2 K_E \phi_{E_0}} \quad (6)$$

and the selectivity ratio is defined as :

$$S_R = S_D / S_0 \quad (7)$$

Effect of diffusion and adsorption on selectivity  
of some complex reactions correlation  
and case study

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398

**A THESIS**

Submitted in Partial Fulfilment of the Requirements

FOR THE DEGREE OF

**MASTER OF TECHNOLOGY**

POST GRADUATE OFFICE  
This thesis has been approved  
for the award of the Degree of  
Master of Technology (M Tech.)  
in accordance with the  
regulations of the Indian  
Institute of Technology Kanpur  
Dated. 2. 9. 70

By

**JAGDISH CHANDER GUPTA**

to the

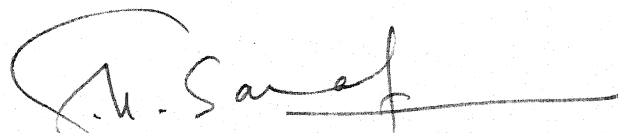
**DEPARTMENT OF CHEMICAL ENGINEERING  
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR**

August 1970

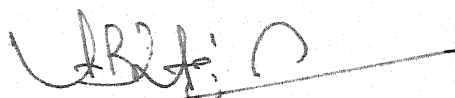


CERTIFICATE

It is certified that this work has been carried out under our supervision and that this has not been submitted elsewhere for a degree.



(Dr.) S.K. Saraf, Sc.D. (MIT)  
Assistant Professor  
Department of Chemical Engineering,  
Indian Institute of Technology  
Kanpur, India



(Dr.) A.B.L. Agarwal, Ph.D. (IIT)  
Department of Chemical Engineering,  
Indian Institute of Technology,  
Kanpur, India

August 10, 1970

POST GRADUATE OFFICE  
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Dated. 2.9.70 24

ACKNOWLEDGEMENT

The author wishes to express his deep sense of gratitude to Dr. S.K. Saraf for his guidance and for the many stimulating discussions during the course of this work.

Thanks are also due to Dr. A.B.L. Agarwal for his help in numerical computations. The author also wishes to thank the Computer Centre of the Indian Institute of Technology, Kanpur for allowing the use of IBM 7044 Computer for numerical computations.

Thanks are also due to Mr. B.S. Pandey for typing the manuscript.

Author

ABSTRACT

The effect of diffusion and adsorption on the selectivity of some complex reactions is studied. All the three reaction types, namely, independent, parallel and series, are studied. The combined effect of various parameters on overall selectivity ratio of the reaction is studied. The dimensionless parameters studied are: modified Thiele parameter,  $\phi_M$ , equilibrium constant for reversible reaction,  $K_1$ , ratio of reaction rate constants,  $K_2$ ,  $K_{Ap_0}$ , diffusivity ratios and adsorption equilibrium constant ratios with respect to reactant A. An attempt is made to correlate the overall selectivity ratio with individual selectivity ratios obtained by Agarwal (1) by varying only one parameter at a time. Multiple regression analysis is used to find the best correlation. Satisfactory correlations are established for independent and series reactions. No simple correlation is possible for parallel reactions.

Thiophene hydrogenolysis reaction, a series of reaction of industrial importance, is chosen for detailed study. Variations in selectivity and product distribution are presented as a function of thiophene conversion for modified Thiele parameter range of 0.2 to 2.0. As expected, the concentration of reaction intermediate is found to decrease with increase in the value of Thiele parameter for a given Thiophene conversion.

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\* \* \*

NOMENCLATURE

a	Constant
a	Constants of the regression equation
A	Component A
A	Constant of the regression equation
A	Thiophene
B	Component B
B	Hydrogen
C	Component C
C	Butene
D	Component D
D	Diffusivity, $\text{cm}^2/\text{sec.}$
D	Hydrogen Sulfide
E	Component E
E	Butane
$k_1, k_2$	Forward Reaction Velocity Constants for Reaction 1 and 2
$k_1$	Reverse Reaction Velocity Constant for Reaction 1
K	Adsorption Equilibrium Constant
$K_1$	Equilibrium Constant for Reversible Reaction
$K_1$	Equilibrium Constant for Irreversible Reaction
$K_2$	Ratio of Reaction Velocity Constants
L	Length of the Pore
p	Partial Pressure
$p_0$	Total Pressure Outside the Pore Mouth
r	Rate of reaction, moles/(unit volume of the catalyst pore)(sec.)
S	Cross Sectional Area of the Pore



$S_0$	Selectivity without diffusion effects
$S_D$	Selectivity with diffusion effects
$S_R$	Selectivity ratio, $S_D/S_0$
$X$	Individual Selectivity Ratio
$X$	Normalized Selectivity Ratio
$Y$	Overall Effect of Selectivity Ratio
$Y$	Overall effect of Normalized Selectivity Ratio
$Z$	Distance Along the Pore

### Greek Letters

$\alpha$	Constant of the rate equations under given conditions
$\beta$	Constant of the rate equations under given conditions
$\gamma$	Constant of the rate equations under given conditions
$\delta$	Constant of the rate equations under given conditions
$\omega$	Constant of the rate equations under given conditions
$\xi$	Constant of the rate equations under given conditions
$\chi$	Constant of the rate equations under given conditions
$\phi$	Dimensionless partial pressure, $p/p_0$
$\eta$	Dimensionless distance along the pore, $z/L$
$\phi_M$	Modified Thiele Parameter
$\Delta$	Increment

### Subscripts

A	Component A
B	Component B
C	Component C
D	Component D
E	Component E
n	Number
O	Condition at the pore mouth

## CHAPTER I

### INTRODUCTION

Many chemical reactions are carried out by contacting a fluid and porous solid that catalyses a reaction involving some constituent of the fluid. Essentially all surface area of a high area catalyst is present in the interior of the catalyst mass. Pores run through the particles in a random, interconnecting fashion. Diffusion of gas or liquid is the predominant mode of mass transfer within the catalyst pellet. In some cases, bulk flow of fluid in the pores or surface migration of adsorbed species might be significant, but diffusion is far more important than either of these transport mechanisms in most high temperature and low pressure catalytic processes. Gaseous diffusion in commercial catalysts is usually either in the Knudsen or transition regime, due to small pore sizes of most high area catalysts. However in very large pores such as occur in low area porous catalysts made by compacting non-porous catalyst particles, bulk diffusion may predominate.

When a reaction takes place in a porous catalyst mass, the fluid reactants have to diffuse inside the catalyst particle to make the effective use of the surface area available

in its pores since most of the surface area is inside the pores as pore walls. The reactants are chemisorbed and then react to form the chemisorbed product. The product molecules are then desorbed and diffuse out of the catalyst particle to the surface from which it is transferred to the bulk of the fluid. Each of these steps offer some resistance and the rate of reaction taking place in a catalyst pore depends upon the magnitude of these resistances. In the past, expressions for the rate of reaction in a catalyst pore were obtained taking into account these resistances. If all these resistances are considered together, the rate expression becomes too much involved and in many cases it is not possible to obtain the rate expression in terms of measurable quantities. For this reason generally it is assumed that out of all these steps, one of them offer maximum resistance and accordingly all others neglected. Thus the rate of reaction equals the rate of the slowest step.

As a result of pore diffusion there exists a concentration gradient inside the pore and hence reaction takes place with different rates at different positions in the catalyst pore. This affects the activity of the catalyst which is expressed in terms of effectiveness factor, defined as the actual rate of reaction divided by the rate of reaction if there is no concentration gradient due to mass transfer limitations. In complex reactions where more than one reaction is taking place, quite often, different reactions are effected

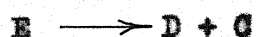
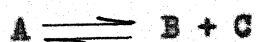
in a different way and there is change in selectivity. The term selectivity is generally defined as the rate of desired reaction divided by the rate of disappearance of the key reactant.

Agarwal (1) studied the effect of diffusion on selectivity of some complex reactions by using Langmuir-Hinshelwood type of rate expressions, which takes into account the effect of adsorption on reaction rates and the results were presented in terms of selectivity ratio as a function of modified Thiele parameter for various reaction parameters. By varying only one variable at a time while keeping all others at a constant value of unity, the effect of different parameters on the selectivity of some complex reaction was presented. However, for any actual reaction the values of most of these parameters may be greatly different from unity and as such the results can not be applied directly.

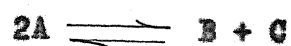
In the present work, an attempt is made to study the effect of interaction of various parameters on selectivity by arbitrarily varying the values of these parameters and to correlate these results with those obtained by Agarwal (1).

The reactions considered for detail study are:

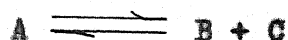
#### 1. Independent Reactions



## 2. Parallel Reactions



## 3. Series Reactions



In each case the first reaction is taken as reversible to consider the effect of reversibility.

The effect of adsorption and diffusion on the selectivity of an industrially important series reaction, namely, thiophene hydrogenolysis is also studied (Appendix B ) and the variation in selectivity is presented as a function of thiophene conversion for selected values of Thiele parameter.

\* \* \*

## CHAPTER II

### LITERATURE REVIEW

Sherwood and Satterfield (2) in their recent book have given an excellent account of the progress made over past three decades since the pioneering work of Damkohler (3), Thiele (4) and Zeldowitch (5) in the general area of the role of diffusion in catalysis.

In catalytic reactions, the rate expressions are not simple first or second order expressions. To account for the effect of adsorption, Langmuir-Hinshelwood type of rate expressions are to be used. For the first time Chu and Hougen (6) considered the effect of adsorption on effectiveness factor by analyzing a first order irreversible reaction  $A \longrightarrow B$ . Roberts and Satterfield (7,8) analyzed the reaction,  $A + bB \longrightarrow \text{products}$ , assuming first and second order irreversible reaction kinetics. Schneider and Mitschka (9, 10, 11, 12) and Kao and Satterfield (13) considered first order reversible reaction,  $A \rightleftharpoons B$  and showed that the retardation effect (due to pore diffusion) is more for reversible reactions than for irreversible reactions.

For complex reactions the effect of pore diffusion selectivity was studied by Wheeler (14) who designated \*

different types of selectivity, since each is affected quite differently by the pore diffusion. Selectivity for independent reactions has been studied by Wheeler (14); for parallel reactions by Ostergaard (15) and Fowloski (16); and for series reactions by Carberry (17), Weiz (5) and Wheeler (14). All of them have considered simple first or higher order reaction kinetics.

Agarwal (1) has studied the effect of diffusion and adsorption on selectivity of some complex reactions in a cylindrical pore without radial gradients using Langmuir-Hinshelwood type of rate expressions to take care of adsorption effects. He assumed that the surface reaction controls the rate of reaction. In this study the effect of pressure gradient, changes in the diffusivities and adsorption equilibrium constants within the pore were neglected. Diffusion with chemical reaction gives rise to a set of non-linear differential equations of the boundary value type whose initial conditions are missing. The solution was achieved by quasi-linearization (18) and invariant imbedding techniques (19).

\* \* \*

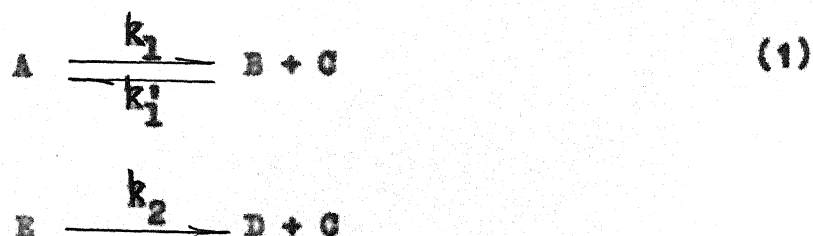
### CHAPTER III

#### MATHEMATICAL FORMULATION OF THE PROBLEM AND THE SOLUTION TECHNIQUES

This chapter presents the important results of the mathematical developments carried out by Agarwal (1) for the sake of continuity and clarity of presentation of the work done by the author.

##### A. Independent Reactions:

When two reactions with different reactants are taking place on a catalyst, the reactions are called independent reactions. The reaction scheme considered for detailed study is same as that of Agarwal (1) and is given below:



If single site mechanism is assumed for both the reactions, where component C is reacting in the gas phase and surface reaction controls the rate of reaction, the rate expressions



for components A and E can be written as

$$\begin{aligned}
 -r_A &= \frac{k_1 K_A (p_A - \frac{p_B p_C}{K})}{(1 + \sum_i K_i p_i)} \\
 -r_E &= \frac{k_2 K_E p_E}{(1 + \sum_i K_i p_i)}
 \end{aligned}
 \tag{2}$$

where  $r_A$  and  $r_E$  are the rate of formation of component A and E per unit pore volume.  $k_1$ ,  $k_1'$  and  $k_2$  are the reaction rate constants for the adsorbed species in the direction indicated in equation (1),  $K_i$  is the adsorption equilibrium constant for component i,  $p_i$  is the partial pressure of component i,  $K$  is the equilibrium constant for the first reaction and subscript i stands for all components present in the reaction mixture viz., A, B, C, D and E. The rate of reaction of other components can be obtained from simple stoichiometry

$$\begin{aligned}
 r_B &= -r_A \\
 r_D &= -r_E \\
 r_C &= r_B + r_D
 \end{aligned}
 \tag{3}$$

with simultaneous diffusion and reaction within the pore, at steady state, the mass balance for any component

$$D_1 \frac{d^2 C_1}{dz^2} = -r_1
 \tag{4}$$

Without going through the details of mathematical development which are explained by Agarwal (1), only the final form of differential equations with dimensionless variables are reproduced below:

$$\frac{d^2 \phi_A}{d\eta^2} = \frac{\phi_M^2 \left[ \phi_A - \left( \alpha - \frac{D_A}{D_B} \phi_A \right) \left( \beta - \frac{D_A}{D_C} \phi_A - \frac{D_E}{D_C} \phi_E \right) / K_1 \right]}{\omega + \gamma \phi_A + \delta \phi_E} \quad (5a)$$

$$\frac{d^2 \phi_E}{d\eta^2} = \phi_M^2 \frac{1}{K_2} \frac{D_A}{D_E} \frac{\phi_E}{(\omega + \gamma \phi_A + \delta \phi_E)} \quad (5b)$$

where  $\phi = p/p_0$

$\eta = z/L$

$$K_1 = K/p_0$$

$$\phi_M = \frac{L}{\sqrt{\frac{K_1 K_A RT}{D_A (1 + K_A p_0)}}}$$

$$\omega = \frac{1}{1 + K_A p_0} + \frac{K_A p_0}{1 + K_A p_0} \left[ \alpha \frac{K_B}{K_A} + \beta \frac{K_C}{K_A} + \frac{K_D}{K_A} \left( \phi_{D_0} + \frac{D_E}{D_D} \phi_{E_0} \right) \right]$$

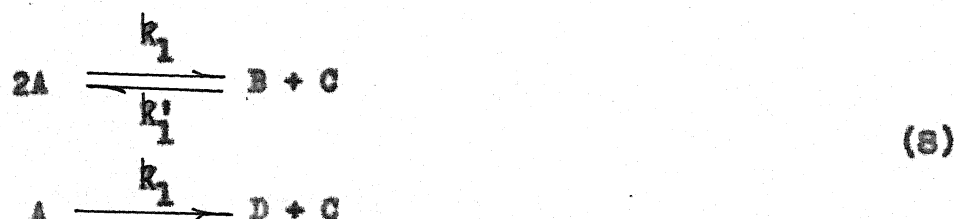
$$\alpha = \phi_{B_0} + \frac{D_A}{D_B} \phi_{A_0}$$

$$\gamma = \frac{K_A p_0}{1 + K_A p_0} \left( 1 - \frac{K_B}{K_A} \frac{D_A}{D_B} - \frac{K_C}{K_A} \frac{D_A}{D_C} \right)$$

To get selectivity ratio, the values of  $\left. \frac{d\phi_A}{d\eta} \right|_{\eta=0}$  and  $\left. \frac{d\phi_E}{d\eta} \right|_{\eta=0}$  are to be obtained which are nothing but the missing initial conditions of the equations (5a) and (5b). The special case studied assumes that the concentration of products at pore mouth is zero and the two reactants are present in equal proportion, that is  $\phi_{B_0} = \phi_{C_0} = \phi_{D_0} = 0$  and  $\phi_{A_0} = \phi_{E_0} = 0.5$ .

### B. Parallel Reactions:

When two or more reactions with same reactants are taking place on a catalyst surface the reactions are called parallel reactions. The reaction scheme considered for study is same as that of Agarwal(1) and is given below:



If dual site mechanism for the first reaction and single site mechanism for the second reaction are assumed, the rate expressions for B and D can be expressed as follows:

$$\begin{aligned}
 r_B &= \frac{k_1 K_A^2 (p_A^2 - \frac{p_B p_C}{K_1})}{(1 + \sum_1 K_1 p_1)^2} \\
 r_D &= \frac{k_2 K_A p_A}{(1 + \sum_1 K_1 p_1)}
 \end{aligned} \quad (9)$$

The rate of reaction of other components can be obtained from simple stoichiometry

$$\begin{aligned} -r_A &= 2 r_B + r_D \\ r_C &= r_B + r_D \end{aligned} \quad (10)$$

Without going through the details, only the final form of differential equation is given below:

$$\begin{aligned} \frac{d^2 \phi_B}{d\eta^2} &= - \frac{\phi_B^2 \left( \frac{D_A}{D_B} \right) \frac{K_A P_0}{1+K_A P_0} \left[ \left( \alpha_1 - 2 \frac{D_B}{D_A} \phi_B - \frac{D_D}{D_A} \phi_D \right)^2 - \frac{\phi_B}{K_1} \left( \beta_1 + \frac{D_B}{D_C} \phi_B + \frac{D_D}{D_C} \phi_D \right) \right]}{(\omega_1 + \gamma_1 \phi_B + \delta_1 \phi_D)^2} \\ \frac{d^2 \phi_D}{d\eta^2} &= - \frac{\phi_D^2 \frac{1}{K_2} \frac{D_A}{D_D} \left( 1 - \frac{2D_B}{D_A} \phi_B - \frac{D_D}{D_A} \phi_D \right)}{(\omega_1 + \gamma_1 \phi_B + \delta_1 \phi_D)} \end{aligned} \quad (11)$$

where

$$\omega_1 = \frac{1}{1+K_A P_0} + \frac{K_A P_0}{1+K_A P_0} \left( \alpha_1 + \frac{K_C}{K_A} \beta_1 \right)$$

$$\gamma_1 = \frac{K_A P_0}{1+K_A P_0} \left( \frac{K_B}{K_A} - \frac{2D_B}{D_A} + \frac{K_C}{K_A} \frac{D_B}{D_C} \right)$$

$$\beta_1 = \phi_{C_0} - \frac{D_B}{D_C} \phi_{B_0} - \frac{D_D}{D_C} \phi_{D_0}$$

$$\delta_1 = \frac{K_A P_0}{1+K_A P_0} \left( \frac{K_D}{K_A} - \frac{D_D}{D_A} + \frac{K_C}{K_A} \frac{D_D}{D_C} \right)$$

$$\alpha_1 = \phi_{A_0} + \frac{2D_B}{D_A} \phi_{B_0} + \frac{D_D}{D_A} \phi_{D_0}$$

With boundary conditions:

$$\text{at } \eta = 0; \phi_B = \phi_{B_0} \text{ and } \phi_D = \phi_{D_0}$$

$$\text{and at } \eta = 1 \quad \frac{d\phi_B}{d\eta} = \frac{d\phi_D}{d\eta} = 0$$

The selectivity with diffusion effects is defined as

$$S_D = \frac{\text{Rate of formation of B within the pore}}{\text{Rate of disappearance of A within the pore}}$$

$$= \frac{\frac{D_B}{D_A} \left. \frac{d\phi_B}{d\eta} \right|_{\eta=0}}{2 \frac{D_B}{D_A} \left. \frac{d\phi_B}{d\eta} \right|_{\eta=0} + \frac{D_D}{D_A} \left. \frac{d\phi_D}{d\eta} \right|_{\eta=0}}$$

The rate of reaction without diffusion effects can be obtained by proper substitution in rate equation (9) to give selectivity without diffusion effects as

$$S_0 = \frac{r_{B_0}}{2r_{B_0} + r_{D_0}} \quad (12)$$

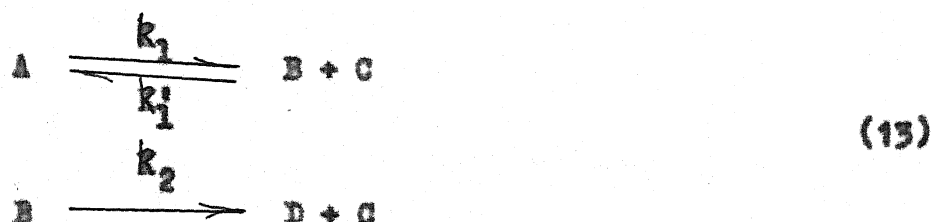
The selectivity ratio is again defined as in equation (7).

The special case studied assumes that the concentration of products at pore mouth is zero and only reactant A is present that is,

$$\phi_{B_0} = \phi_{C_0} = \phi_{D_0} = 0 \text{ and } \phi_{A_0} = 1.$$

### C. Series Reactions

When the product of a reaction further reacts to form a new product (s), the reactions are called series reactions. The reaction scheme considered for detailed study is same as that of Agarwal (1) and given below:



If single site mechanism is assumed for both the reactions with C reacting in the gas phase and also if surface reaction controls the rate of reaction, the following rate expressions can be obtained for the component B and D:

$$\begin{aligned}
 r_B &= \frac{k_1 K_A (p_A - \frac{p_B p_C}{K}) - \frac{p_B}{K_2}}{(1 + \sum_i K_i p_i)} \\
 r_D &= \frac{k_2 K_B p_B}{(1 + \sum_i K_i p_i)} \quad (14)
 \end{aligned}$$

where  $K = \frac{k_1 K_A}{k_1' K_B}$  and

$$K_2 = k_1 K_A / k_2 K_B$$

The rate of other components can be obtained from simple stoichiometry

$$\begin{aligned}
 -r_A &= r_B + r_D \\
 r_C &= -r_A + r_D
 \end{aligned} \quad (15)$$

The final expressions after proper substitutions and simplifications are as follows:

$$\frac{d^2 \phi_B}{d\eta^2} = - \frac{\phi_M^2 \frac{D_A}{D_B} \left[ \alpha_2 - \left( \frac{D_B}{D_A} + \frac{\beta_2}{K_1} + \frac{1}{K_2} \right) \phi_B - \frac{D_D}{D_A} \phi_D - \frac{\phi_B}{K_1} \left( \frac{D_B}{D_C} \phi_B + \frac{2D_D}{D_C} \phi_D \right) \right]}{(\omega_2 + \gamma_2 \phi_B + \delta_2 \phi_D)}$$

$$\frac{d^2 \phi_D}{d\eta^2} = - \phi_M^2 \frac{1}{K_2} \frac{D_A}{D_D} \frac{\phi_B}{(\omega_2 + \gamma_2 \phi_B + \delta_2 \phi_D)} \quad (16)$$

where

$$\omega_2 = \frac{1}{1+K_A p_0} + \frac{K_A p_0}{1+K_A p_0} \left( \alpha_2 + \frac{K_C}{K_A} \beta_2 \right)$$

$$\gamma_2 = \frac{K_A p_0}{1+K_A p_0} \left( \frac{K_B}{K_A} - \frac{D_B}{D_A} + \frac{K_C}{K_A} \frac{D_B}{D_C} \right)$$

$$\delta_2 = \frac{K_A p_0}{1+K_A p_0} \left( \frac{K_D}{K_A} - \frac{D_D}{D_A} + \frac{2K_C}{K_A} \frac{D_D}{D_C} \right)$$

$$\alpha_2 = \phi_{A_0} + \frac{D_B}{D_A} \phi_{B_0} + \frac{D_D}{D_A} \phi_{D_0}$$

$$\beta_2 = \phi_{C_0} - \frac{D_B}{D_C} \phi_{B_0} - \frac{2D_D}{D_C} \phi_{D_0}$$

The rate of reaction without diffusion effects can be obtained by proper substitution in rate equation (14) to give selectivity without diffusion effects as

$$S_0 = \frac{r_B}{r_B + r_D} \quad (17)$$

and the selectivity ratio will again be defined by equation (7).

The special case studied assumes  $\phi_{B_0} = \phi_{C_0} = \phi_{D_0} = 0$  and  $\phi_{A_0} = 1$  as in the case of parallel reaction scheme.

#### D. Solution of a System of Non Linear Boundary Value Problems:

Agarwal (1) used the following two different techniques for the determination of initial missing conditions for a system of non linear boundary value problem.

1. Quasi-Linearization Method
2. Invariant Imbedding Technique

The Quasi-Linearization technique gives reliable results for the entire Thiele parameters range studied, where as the invariant imbedding technique was found to be particularly useful for low Thiele parameter data. The advantage of invariant imbedding technique is that it takes much less time in comparison to that taken by quasi-linearization technique.

In the present study more general programme for each of the two techniques was developed for all different types of reactions schemes mentioned earlier. It was thus possible to study the effect on selectivity of these reaction systems for arbitrarily chosen values of different variable defining the system. The restriction of varying only one variable at a time was removed. These results were used to establish some reasonable correlation to predict the selectivity ratio for a general system where most or all of the variables have



values different from unity, from the selectivity ratio data of Agarwal (1) where only one variable was varied at a time while keeping the value of all other variables at unity.

\* \* \*

## CHAPTER IV

### CORRELATION OF DATA

#### A. Analysis of the Interaction of Various Parameters:

In this chapter, the interaction of various reaction parameters and the consequent influence on overall selectivity of the reaction for a given value of modified Thiele parameter is analyzed. Agarwal (1) has presented his results in terms of selectivity ratio, as a function of modified Thiele parameter for various reaction parameters, by varying only one variable at a time while keeping all others at a constant value of unity. To estimate the overall effect for a system with arbitrarily assigned values of different parameters from the one parameter data of Agarwal (1), the most logical correlation may be to assume that the combined effect on overall selectivity ratio is obtained by taking the product of individual selectivity ratios obtained by varying single parameter. To fit the data each of the individual selectivity ratio are raised to a constant power that is

$$Y = A_0 (X_1)^{a_1} (X_2)^{a_2} \dots (X_n)^{a_n} \quad (18)$$

and the values of these constants,  $a_0$  to  $a_n$ , are to be determined using multiple regression method. The correlation can be done in one of the following two ways:

(i) Y represents combined and  $X_1$  to  $X_n$  represent individual selectivity ratios as such

(ii) Y represents combined and  $X_1$  to  $X_n$  represent individual selectivity ratios each after dividing by the selectivity ratio value when all parameters except Thiele parameter (the value of which is taken as that of the actual system), are taken as unity.

The equation 18 can be written in algebraic form which is amenable to regression analysis simply by taking the logarithm to give

$$\ln Y = A_0 + a_1 \ln X_1 + a_2 \ln X_2 + \dots + a_n \ln X_n \quad (19)$$

The latter method was found to be more promising and was, therefore, chosen for detailed study. A careful study of the results of Agrawal (1) indicated that not all variable parameters have significant influence on selectivity ratio value. It was therefore found desirable to include only those variables, which were observed to influence the selectivity ratio significantly.

#### B. Multiple Regression Analysis:

Regression analysis (22) is designed to examine the relationship between Y to a variable X. Here X is independent variable and is assumed to have no error associated with it. This variable is selected arbitrarily for the purpose of studying Y. Y is a dependent variable and the relationship between X and

is such that

$$Y_i = A + B X_i + \epsilon_i$$

where A and B are parameters of the population and  $\epsilon_i$  is a random variable ( deviation from a population or true line of regression) with mean zero while the X values are selected by the researcher.

The model of interest is

$$y = a_0 + a_1 x_1 + a_2 x_2 + \dots + a_n x_n \quad (20)$$

where  $y = \ln Y$ ,  $a_0 = \ln A_0$ ,  $x_i = \ln X_i$ ,  $i = 1$  to  $n$ .

For finding the constants, least square method assures us that sum of the squares of the vertical deviations from the fitted line will be less than the sum of the squares of the vertical deviations from any other line, no matter how computed. For finding a's we minimize the sum of squares of deviations,

$$\sum \left[ y - (a_0 + a_1 x_1 + a_2 x_2 + \dots + a_n x_n) \right]^2$$

differentiating with respect to  $a_1$  and equating to zero we get first equation and when differentiated with respect to  $a_2, \dots, a_n$  the succeeding equations are obtained. These are called normal equations. For the validity of the final results, the resulting residual sum of squares should be zero that is  $\sum (y - \bar{y}_x) = 0$  where  $y$  is the true value and  $\bar{y}_x$  is the computed value, that is, regression sum of squares equals total sum of squares. This provides a measure of the degree to which the dependent variable is influenced by the  $n$  independent variables.

## CHAPTER V

### RESULTS AND DISCUSSIONS

The following dimensionless variables are studied for their interaction on selectivity ratio

- Modified Thiele parameter,  $\phi_M$
- Reaction equilibrium constant,  $K_1$
- Ratio of reaction velocity constants,  $K_2$
- $K_A P_0$
- Ratio of diffusivities,  $\frac{D_B}{D_A}$ ,  $\frac{D_C}{D_A}$ ,  $\frac{D_D}{D_A}$ ,  $\frac{D_E}{D_A}$
- Ratio of adsorption equilibrium constants,  $\frac{K_B}{K_A}$ ,  $\frac{K_C}{K_A}$ ,  $\frac{K_D}{K_A}$ ,  $\frac{K_E}{K_A}$

that is, the no. of variables studied, excluding modified Thiele parameter are eleven for independent reactions and nine for parallel as well as series reactions. The range of the values of each of the variables is given in the following Table 1

**TABLE 1: Range of the Values of the Variables Studied**

Variable	Range		
$\phi_M$	0.4	-	4.0
$K_1$	0.1	-	100
$K_2$	0.1	-	10
$K_A P_0$	0.01	-	100
$D_B/D_A, D_C/D_A, D_D/D_A, D_E/D_A$	0.25	-	4.0
$K_B/K_A, K_E/K_A$	0.25	-	4.0
$K_C/K_A, K_D/K_A$	0.0	-	4.0

Modified Thiele parameter,  $\phi_M$  is defined as  $L \sqrt{\frac{K_1 K_A RT}{D_A (1+K_A P_0)}}$

A. INDEPENDENT REACTIONS:

Table 2 shows the maximum range of variation of normalized selectivity ratio for all the eleven dimensionless parameters and, in general, corresponds to the variation at the highest value of Thiele parameter as reported by Agarwal (1). 'Appreciable' in remark column of the Table 2 indicates that this variable has significant effect and is included for regression analysis. The variables with "negligible" effect are not used in regression analysis and the value of  $a_i$  for these variables is assumed to be unity.

TABLE 2: Maximum Variations in Normalized Selectivity Ratio

Variable	Normalized*maximum selectivity ratio variation.	Remarks
$K_1$	0.625 — 1.21	Appreciable
$K_2$	0.345 - 2.94	Appreciable
$K_A P_0$	0.99 - 1.005	Negligible
$D_B/D_A$	0.79 - 1.15	Appreciable
$D_C/D_A$	0.81 - 1.14	Appreciable
$D_D/D_A$	0.99 - 1.01	Negligible
$D_E/D_A$	0.5 - 2.11	Appreciable
$K_B/K_A$	0.99 - 1.02	Negligible
$K_C/K_A$	0.98 - 1.04	Negligible
$K_D/K_A$	0.98 - 1.03	Negligible
$K_E/K_A$	0.98 - 1.02	Negligible

\*All the selectivity ratio values are divided by the selectivity ratio value when all the variable parameters, except Thiele parameter, are at unity.

Table 2 indicates that variable parameters  $K_{Ap_0}$ ,  $D_D/D_A$ ,  $K_B/K_A$ ,  $K_C/K_A$ ,  $K_D/K_A$  and  $K_E/K_A$  have very small influence on the selectivity ratio and only the following parameters need detailed study for their influence:

$$K_1, K_2, D_B/D_A, D_C/D_A \text{ and } D_E/D_A.$$

Using the generalized programme, Appendix A, the overall selectivity ratio was calculated for arbitrarily chosen values of parameters  $K_1$ ,  $K_2$ ,  $D_B/D_A$ ,  $D_C/D_A$  and  $D_E/D_A$  at modified Thiele parameter values of 0.4, 0.7, 1, 2 and 4. The values of individual selectivity ratio corresponding to the single parameter variation only at the same Thiele parameter were obtained from the studies of Agrawal(1). Taking a sample size of 164 data points selected randomly, the regression analysis resulted in the best fit with the following values of the constants in equation 18 page 18.

$$\begin{aligned} A_0 &= 0.93 \\ a_1 &= 1.42 \\ a_2 &= 0.95 \\ a_3 &= 1.17 \\ a_4 &= 1.16 \\ a_5 &= 1.06 \end{aligned}$$

where subscript 1,2,3,4 and 5 refer respectively to variable parameters  $K_1$ ,  $K_2$ ,  $D_B/D_A$ ,  $D_C/D_A$  and  $D_E/D_A$ . As indicated earlier all other  $a_i$  corresponding to the remaining variables are taken as unity since their influence on selectivity ratio is small.

The error distribution analysis for 164 random observations taken at the Thiele parameter range of 0.4 to 4 is given in Table 3.

This error distribution shows that nearly eightysix percent of the observations are within thirty percent error of the true calculated value of the overall selectivity ratio. The variation in the calculated value of overall selectivity ratio was observed in the range of 0.3 to 3.6 for the data samples investigated

#### B. SERIES REACTIONS

Table 4 shows the maximum range of the variation of normalized selectivity ratio for all the nine dimensionless parameters and, in general, corresponds to the variation at the highest value of Thiele parameter as reported by Agarwal (1). 'Appreciable' in remark column of the Table 4 indicate that this variable has significant effect and is included for regression analysis. The variables with "negligible" effect are not used in regression analysis and the value of  $a_1$  for these variables is assumed to be unity.

Table 4 indicates that variable parameters  $D_D/D_A$  and  $K_D/K_A$  have very small influence on the selectivity ratio and only the following parameters need detailed study for their relative influence

$K_1$ ,  $K_2$ ,  $K_A P_0$ ,  $D_E/D_A$ ,  $D_C/D_A$ ,  $K_B/K_A$  and  $K_C/K_A$ . Using the generalized program, Appendix A, the overall selectivity ratio was calculated for arbitrarily chosen values of parameters  $K_1$ ,  $K_2$ ,  $K_A P_0$ ,



TABLE 3: DISTRIBUTION ANALYSIS FOR INDEPENDENT REACTIONS

Observations within	For 27 obser- vations at $\phi_M = .4$		For 37 observations at $\phi_M = 1.0$		For 26 obser- vations at $\phi_M = 4$	For 164 obser- vations at $\phi_M = .4, .7, 1, 2, & 4$
	$\phi_M = .7$	$\phi_M = 2$	$\phi_M = 1.0$	$\phi_M = 2$		
five percent error	11	11	6	7	8	43
five to ten percent error	7	8	7	2	6	30
ten to twenty percent error	4	5	11	13	9	42
twenty to thirty percent error	3	7	5	8	2	25
thirty to forty percent error	1	2	2	2	-	7
forty to fifty percent error	-	1	2	3	1	7
Observations with greater than fifty percent error	1	3	4	2	-	10

TABLE 4: Maximum Variations in Normalized Selectivity Ratio

Variable	Normalized maximum selectivity ratio variation			Remarks
$K_1$	0.98	-	1.17	Appreciable
$K_2$	0.45	-	1.38	Appreciable
$K_A / p_O$	0.93	-	1.05	Appreciable
$D_B / D_A$	0.69	-	1.29	Appreciable
$D_C / D_A$	0.93	-	1.13	Appreciable
$D_D / D_A$	0.98	-	1.04	Negligible
$K_B / K_A$	0.95	-	1.05	Appreciable
$K_C / K_A$	0.93	-	1.12	Appreciable
$K_D / K_A$	0.98	-	1.03	Negligible

$D_B / D_A$ ,  $D_C / D_A$ ,  $K_B / K_A$  and  $K_C / K_A$  at modified Thiele parameter values of 0.4, 0.7, 1, and 2. The values of individual selectivity ratio corresponding to the single parameter variation only at the same Thiele parameter are obtained from the studies of Agrawal (1). Taking a sample size of 71 data points selected randomly, the regression analysis resulted in the best fit with the following values of the constants in equation 18 page 18

$$\begin{aligned}
 A_0 &= 0.99 \\
 a_1 &= -0.14 \\
 a_2 &= 1.13 \\
 a_3 &= 0.19 \\
 a_4 &= 1.02
 \end{aligned}$$

$$\begin{aligned}
 a_5 &= 2.38 \\
 a_6 &= 2.01 \\
 a_7 &= 1.86
 \end{aligned}$$

where subscript 1,2, --- and 7 refer respectively to variable parameters  $K_1$ ,  $K_2$ ,  $K_{Ap_0}$ ,  $D_B/D_A$ ,  $D_C/D_A$ ,  $K_B/K_A$ ,  $K_C/K_A$ . As indicated earlier all other  $a_i$  corresponding to the remaining variables are taken as unity since their influence on selectivity ratio is small.

The error distribution analysis for 71 random observations at the Thiele parameter range of 0.4 to 2 is given in Table 5

TABLE 5: Distribution Analysis for Series Reactions

Error Distribution within	For 19 observations at $\phi_M = .4$	For 17 observations		For 18 observations at $\phi_M = 2$	For 71 observations at $\phi_M = .4, .7, 1 \text{ \& } 2$
		at $\phi_M = .7$	at $\phi_M = 1$		
five percent error	9	5	3	6	23
five to ten percent error	8	6	6	10	30
ten to twenty percent error	2	5	8	2	17
twenty to thirty percent error	-	1	-	-	1

The error distribution shows that nearly ninety nine percent of the observations are within twenty percent error of the true calculated value of the overall selectivity ratio. The variation in the calculated value of overall selectivity ratio was observed in the range of 0.4 to 1.45 for data samples investigated.

### C. PARALLEL REACTIONS

The Table 6 shows the maximum range of the variation of normalized selectivity ratio for all the nine dimensionless parameters, and, in general corresponds to the variation at the highest value of Thiele parameter as reported by Agrawal (1).

'Appreciable' in remark column of the Table 6 indicates that this variable has significant effect and is included for regression analysis. The variables with 'negligible' effect are not used in regression analysis and the value of  $a_1$  for these variables is assumed to be unity.

TABLE 6: Maximum Variations in Normalized Selectivity Ratio

Variable	Normalized maximum selectivity ratio variation			Remarks
$K_1$	0.785	-	1.07	Appreciable
$K_2$	0.723	-	1.485	Appreciable
$K_A p_0$	0.91	-	1.085	Appreciable
$D_B / D_A$	0.89	-	1.05	Appreciable
$D_C / D_A$	0.91	-	1.07	Appreciable
$D_D / D_A$	0.98	-	1.05	At a lower Thiele parameter, Appreciable
$K_B / K_A$	0.995	-	1.00	Negligible
$K_C / K_A$	0.97	-	1.05	At a lower Thiele parameter, Appreciable
$K_D / K_A$	0.975	-	1.05	-do-

It is observed from the Table 6 that variation of the ratio of selectivity ratio is almost negligible for  $K_B / K_A$ . Though the

variations of  $D_D/D_A$ ,  $K_C/K_A$  and  $K_D/K_A$  are also very small at the highest available Thiele parameter but the variations at lower Thiele parameter are appreciable, these are, therefore, taken into the analysis. In this case since the combined selectivity ratio was found to vary over a very wide range of 0.04 to 12.5, it was not possible to use the same constants over the entire range of Thiele parameter, so as to obtain a generalized expression to calculate combined selectivity ratio with reasonable accuracy. Using the multiple regression analysis separately for each Thiele parameter region, that is low ( $\phi_M = 0.4$ ), moderate ( $\phi_M = 0.7$  and 1) and high ( $\phi_M = 2$  and 4) the following values of constants (Table 7) were obtained. The results are tabulated below for all the three cases in Table 7.

TABLE 7: Values of Constants for Parallel Reactions

Parameter	Constant	Value of Constant for Thiele Parameter		
		Value of		
		$\phi_M = 0.4$	$\phi_M = 0.7$ and 1	$\phi_M = 2$ and 4
	$A_0$	1.11	2.85	0.97
$K_1$	$a_1$	38.7	-3.33	0.66
$K_2$	$a_2$	-0.67	1.4	0.87
$K_A P_0$	$a_3$	-4.15	0.27	0.82
$D_B/D_A$	$a_4$	131.5	12.35	-17.7
$D_C/D_A$	$a_5$	20.0	-25.37	4.38
$D_D/D_A$	$a_6$	62.7	57.5	64.34
$K_C/K_A$	$a_7$	9.02	3.84	-9.22
$K_D/K_A$	$a_8$	4.37	0.04	25.92

In view of the large values of constants as determined by the regression analysis, the usefulness of equation 18 page 18 to predict the combined selectivity ratio is open to serious doubts. The error distribution analysis for three ranges of Thiele parameter is given in Table 8.

Using these values of constants, even though seventy five percent 'data points' of low Thiele parameter range, ninety percent data points of moderate Thiele parameter range and ninety five percent data points of high Thiele parameter range lie within thirty percent error, the applicability of equation 18, page 18, to predict overall selectivity ratio value is not recommended because of the large values of these constants.

TABLE 8: Error Distribution Analysis for Parallel Reactions

Observations within	For 53 obs- vations at $\phi_M = .7$	For 39 obs- vations at $\phi_M = 1$	For 92 obs- vations at $\phi_M = .7$ and 1	For 29 obs- vations at $\phi_M = 2$	For 10 obs- vations at $\phi_M = 4$	For 39 obs- vations at $\phi_M = 2$ and 4	For 18 obs- vations at $\phi_M = 0.4$
five percent error	7	2	9	12	4	16	3
five to ten percent error	12	2	14	6	3	9	5
ten to twenty percent error	25	13	38	8	1	9	4
twenty to thirty percent error	5	16	21	3	-	3	1
thirty to forty percent error	4	6	10	-	-	-	2
forty to fifty percent error	-	-	-	-	-	-	1
observations with greater than fifty percent error	-	-	-	-	2	2	2

## CHAPTER VI

### CONCLUSIONS AND RECOMMENDATIONS

#### A. Conclusions:

1. All the dimensionless parameters do not effect the reaction selectivity to same degree. The dimensionless parameters having significant influence are:

a. Independent Reactions: reaction equilibrium constant  $K_1$ , ratio of reaction rate constant  $K_2$ , and diffusivity ratios  $D_B/D_A$ ,  $D_C/D_A$  and  $D_E/D_A$ .

b. Series Reaction:  $K_1$ ,  $K_2$ ,  $K_{AP_0}$ ,  $D_B/D_A$ ,  $D_C/D_A$ , and adsorption equilibrium constant ratios  $K_B/K_A$  and  $K_C/K_A$ .

c. Parallel Reaction: All parameters except  $K_B/K_A$ .

2. Satisfactory correlations to estimate the overall selectivity ratio from individual selectivity ratios (obtained by varying at a time only one parameter) are found for independent and series reactions. For series reactions ninety nine percent of the seventy one data points are found to lie within twenty percent of the true calculated value. For independent reactions eighty five percent of the 164 data points are found to lie within thirty percent.

3. No single correlation is found to be applicable for parallel reactions in the entire range of Thiele parameter studied. Furthermore some of the computed values of the constants for use in correlations are very large and unrealistic.



4. The study of Thiophene hydrogenolysis showed that the selectivity and product distribution was significantly influenced by thiophene conversion and Thiele parameter. Increase in the value of Thiele parameter reduced the concentration of reaction intermediate. Increase in conversion also showed a similar effect on product distribution.

**B. Recommendations:**

1. Correlations to predict overall selectivity from individual selectivity, even though useful to estimate the relative effect of various parameters on overall selectivity, may not provide the complete answer, and individual reaction scheme may be studied separately using the generalized programme with actual values of various reaction parameter.

2. The technique developed is of great practical value and the application can be extended to other industrially important reactions.

\* \* \*

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# APPENDIX A1

```

$JOB CGG094,TIME008,PAGES030,NAME J.C.GUPTA
$IBJOB
$IBFTC
      DIMENSION X(1000),Y(1000),H(1000),E(1000),P(1000),Q(1000),C(1000),
      1 PP(1000),QQ(1000),GG(1000),R(1000),S(1000),V(1000),W(1000),B(50)
C      GENERAL PROGRAMME FOR INDEPENDENT REACTIONS USING
C      QUASI LINEARIZATION TECHNIQUE
C      FOR EFFECT OF DIFFUSION AND ADSORPTION ON SELECTIVITY
C      OF SOME COMPLEX REACTIONS
130  FORMAT(/2X,120(1H-))
      CALL FLOV(10000)
      C=.1E+07
11  READ1,A,(B(I),I=1,11)
1  FORMAT(12F6.2)
      ITERAT=0.
      XO=0.
      YO=0.
      DO 2 I=1,1000
      X(I)=0.001
2  Y(I)=0.001
      BB95=B(9)/B(5)
      BB84=B(8)/B(4)
      BB97=B(9)/B(7)
      BB133=1./(1.+B(3))
      BB76=B(7)/B(6)
      BB74=B(7)/B(4)
      BB27=1./(B(7)*B(2))
      BB313=B(3)/(1.+B(3))
      BB45=1./(B(4)*B(5))
      BB745=(B(7))/(B(4)*B(5))
      BB75=B(7)/B(5)
      BB5=1./B(5)
      BB145=B(1)*B(4)*B(5)
      BB17=1.+B(7)
      BB4=1./B(4)
      PRINT 130
7  ITERAT=ITERAT+1
      CALL FLUN(30000)
      DO 3 I=1,999
      R(I)=(A*A/BB145)*(BB145*X(I)-(0.5-X(I))*(0.5*BB17-X(I)-Y(I)*B(7)))
      S(I)=
      1BB133+BB313*.5*(BB84+BB17*BB95+BB76*B(10))+BB313*((1.-BB84-BB95)*
      2X(I)+Y(I)*(B(11)-B(9)*BB75 B(10)*BB76))
      H(I)=-(2.*C-(R(I)*BB313*(1.-BB84-BB95)/S(I)**2)+(A*A/BB145)*

```



```

1(BB145+0.5+0.5*BB17-2.*X(1)-B(7)*Y(1))/S(1)
E(1)=-(2.*C-(A*A*BB27*Y(1)*BB313*(B(11)-B(9)*BB75-B(10)*BB761))/(S
1(1)*S(1))+(A*A*BB27)/S(1))
V(1)=(R(1)/S(1))+X(1)*(H(1)+2.*C)
W(1)=(A*A*BB27*Y(1)/S(1))+Y(1)*(E(1)+2.*C)
3 CONTINUE
W(1)=W(1)-.5*C
V(1)=V(1)-0.5*C
H(999)=H(999)+C
E(999)=E(999)+C
P(1)=H(1)
Q(1)=C/P(1)
G(1)=V(1)/P(1)
PP(1)=E(1)
QQ(1)=C/PP(1)
GG(1)=W(1)/PP(1)
DO 4 I=2,999
P(I)=H(I)-C*Q(I-1)
Q(I)=C/P(I)
G(I)=(V(I)-C*G(I-1))/P(I)
PP(I)=E(I)-C*QQ(I-1)
QQ(I)=C/PP(I)
GG(I)=(W(I)-C*GG(I-1))/PP(I)
4 CONTINUE
X(999)=G(999)
Y(999)=GG(999)
DO 5 I=1,998
M=999-I
X(M)=G(M)-Q(M)*X(M+1)
5 Y(M)=GG(M)-QQ(M)*Y(M+1)
X1=(X(1)-.5)*1000.
Y1=(Y(1)-.5)*1000.
IF(ABS(X0-X1)-.001)15,15,16
15 IF(ABS(Y0-Y1)-.001)17,17,16
16 X0=X1
Y0=Y1
IF(ITERAT.GT.10) GO TO 11
GO TO 7
17 AB=(X1*BB27)/Y1
PRINT8,A,(B(I),I=1,11),X1,Y1,AB
8 FORMAT(12F6.2,8X,3E16.8)
GO TO 11
111 STOP
END
SENTRY

```



# APPENDIX A2

JOB CGG094, TIME008, PAGES020, NAME J.C.GUPTA

12 JOB  
13 BFTC

```

1  DIMENSION X(1000),Y(1000),H(1000),E(1000),P(1000),Q(1000),S(1000),
2  PP(1000),QQ(1000),GG(1000),R(1000),V(1000),W(1000),B(50)
3  GENERAL PROGRAMME FOR SERIES REACTIONS USING
4  QUASI LINEARIZATION TECHNIQUE
5  FOR EFFECT OF DIFFUSION AND ADSORPTION ON SELECTIVITY
6  OF SOME COMPLEX REACTIONS
7
8  FORMAT(/2X,120(1H-))
9  C=.1E+07
10 READ 1,A,(B(I),I=1,9)
11 FORMAT(10F7.2)
12 ITERAT=0
13 XO=0.
14 YO=0.
15 DO 2 I=1,1000
16 X(I)=0.001
17 Y(I)=.001
18 PRINT130
19 ITERAT=ITERAT+1
20 SS= B(8)*B(4)/B(5)
21 FAC=B(3)/(1.+B(3))
22 DO 3 I=1,999
23 R(I)=(-A*A/B(4))*(1.-(B(4)+1./B(2))*X(I)-B(6)*Y(I)-(X(I)*B(4)/B(5)
24 +2.*B(6)*Y(I)/B(5))*X(I)/B(1))
25 S(I)=1.+FAC*((B(7)-B(4)+SS)*X(I)+(B(9)-B(6)+(2.*
26 1B(8)*B(6))/B(5))*Y(I))
27 H(I)=-((2.*C+(-A*A/B(4))*(-(B(4)+1./B(2))-(2.*X(I)*B(4)/B(5)+2.*
28 1B
29 2(6)*Y(I)/B(5))*1./B(1))/S(I)-(R(I)*FAC*(B(7)-B(4)+ B(8)*B(4)/B(
30 35)))/S(I)**2)
31 E(I)=-((2.*C+
32 1 (A*A*X(I))/(B(2)*P(6))*(B(9)-B(6)+2.*B(8)*B(6)
33 2/B(5))*FAC/S(I)**2)
34 V(I)=(R(I)/S(I))+X(I)*(H(I)+2.*C)
35 W(I)=(-A*A*X(I))/(B(2)*B(6)*S(I))+Y(I)*(E(I)+2.*C)
36 CONTINUE
37 H(999)=H(999)+C
38 E(999)=E(999)+C
39 P(1)=H(1)
40 Q(1)=C/P(1)
41 G(1)=V(1)/P(1)
42 PP(1)=E(1)
43 QQ(1)=C/PP(1)
44 GG(1)=W(1)/PP(1)
45 DO 4 I=2,999
46 P(I)=H(I)-C*Q(I-1)

```

```

G(I)=(V(I)-C*G(I-1))/P(I)
PP(I)=E(I)-C*QQ(I-1)
QQ(I)=C/PP(I)
GG(I)=(W(I)-C*GG(I-1))/PP(I)
4  CONTINUE
X(999)=G(999)
Y(999)=GG(999)
DO 5 I=1,998
M=999-I
X(M)=G(M)-Q(M)*X(M+1)
5  Y(M)=GG(M)-QQ(M)*Y(M+1)
X1=1000.*X(1)
Y1=1000.*Y(1)
IF(ABS(X0-X1)-.001)15,15,16
15 IF(ABS(Y0-Y1)-.001)17,17,16
16 X0=X1
Y0=Y1
IF(ITERAT.GT.25) GO TO 11
GO TO 7
17 AB=B(4)*X1/(B(4)*X1+B(6)*Y1)
PRINT 8,A,(B(I),I=1,9),X1,Y1,AB
8  FORMAT(10F6.2,8X,3E16.8)
GO TO 11
111 STOP
END
SENTRY

```



# APPENDIX A3

```

$JOB CGG094,TIME008,PAGES020,NAME J.C.GUPTA PARALLEL
$IBJOB
$IBFTC
  DIMENSION X(1000),Y(1000),H(1000),E(1000),P(1000),Q(1000),G(1000),
1 PP(1000),QQ(1000),GG(1000),R(1000),S(1000),V(1000),W(1000),B(50)
C GENERAL PROGRAMME FOR PARALLEL REACTIONS USING
C QUASI LINEARIZATION TECHNIQUE
C FOR EFFECT OF DIFFUSION AND ADSORPTION ON SELECTIVITY
C OF SOME COMPLEX REAC
130 FORMAT(/2X,120(1H-))
  C=.1E+07
11 READ1,A,(B(I),I=1,9)
1 FORMAT(10F7.2)
  ITERAT=0
  XO=0.
  YO=0.
  DO 2 I=1,1000
  X(I)=.01
2 Y(I)=.01
  PRINT 130
7 ITERAT=ITERAT+1
  SS4=B(7)-2.*B(4)+B(8)*F(4)/B(5)
  SS5=B(9)-B(6)+B(8)*B(6)/B(5)
  DY1=A*A/B(2)
  DY2=FAC*(B(9)-B(6)+B(8)*B(6)/B(5))
  AA=-A*A*B(3)/(B(4)*(1.+B(3)))
  FAC=B(3)/(1.+B(3))
  SS2=2.*SS4*FAC
  DO 3 I=1,999
  R(I)=AA*((1.-2.*B(4)*X(I)-B(6)*Y(I))*2-(B(4)*X(I)/B(5)+B(6)*Y(I)/
1 B(5))*(X(I)/B(1)))
  SS1=(1.+FAC*(SS4*X(I)+Y(I)*SS5))
  RR=-(A*A/(B(2)*B(6)))*(1.-2.*B(4)*X(I)-B(6)*Y(I))
  S(I)=(1.+FAC*(SS4*X(I)+Y(I)*SS5))*2
  DX1=2.*(1.-2.*B(4)*X(I)-B(6)*Y(I))
  DX2=-DX1*2.*B(4)
  DX3=(2.*X(I)*B(4)/B(5)+B(6)*Y(I)/B(5))*(1./B(1))
  H(I)=-(2.*C+(S(I)*AA*(DX2-DX3)-R(I)*SS1*SS2)/S(I))*2
  E(I)=-(2.*C+(SS1*DY1-RR*FAC*SS5)/S(I))
  V(I)=(R(I)/S(I))+X(I)*(2.*C+H(I))
  W(I)=(RR/SS1)+Y(I)*(2.*C+E(I))
3 CONTINUE
  H(999)=H(999)+C

```



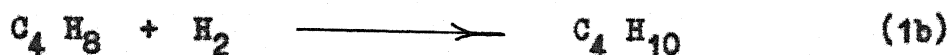
```

E(999)=E(999)+C
P(1)=H(1)
Q(1)=C/P(1)
G(1)=V(1)/P(1)
PP(1)=E(1)
QQ(1)=C/PP(1)
GG(1)=W(1)/PP(1)
DO 4 I=2,999
P(I)=H(I)-C*Q(I-1)
Q(I)=C/P(I)
G(I)=(V(I)-C*G(I-1))/P(I)
PP(I)=E(I)-C*QQ(I-1)
QQ(I)=C/PP(I)
4 GG(I)=(W(I)-C*GG(I-1))/PP(I)
X(999)=G(999)
Y(999)=GG(999)
DO 5 I=1,998
M=999-I
X(M)=G(M)-Q(M)*X(M+1)
5 Y(M)=GG(M)-QQ(M)*Y(M+1)
X1=X(1)*1000.
Y1=Y(1)*1000.
IF(ABS(X0-X1)-.001)15,15,16
15 IF(ABS(Y0-Y1)-.001)17,17,16
16 X0=X1
Y0=Y1
IF(ITERAT.GT.25) GO TO 11
GO TO 7
17 AB=(1.+B(3)*(1.+2.*B(2)))*B(6)* X1 /(B(2)*B(3)*(2.*B(4)* X1 +B(
16)*Y1))
PRINT 8,A,(B(I),I=1,9),X1,Y1,AB
8 FORMAT(10F6.2,8X,3E16.8)
GO TO 11
111 STOP
END
$ENTRY

```

APPENDIX BTHIOPHENE HYDROGENOLYSIS: EFFECT OF DIFFUSION  
LIMITATION ON PRODUCT DISTRIBUTIONB.1 General Reaction Mechanism:

The kinetics of thiophene hydrogenolysis was studied by Roberts (20) over a cobalt molybdate catalyst in a differential reactor with recirculation, the total pressure was about one atmosphere and temperature range 235 - 265 °C. The reaction proceeds as follows:



This hydrogenolysis of thiophene is of the form A B C. In this case, reaction rate was inhibited by a reaction product, hydrogen sulfide. The rate expression for thiophene disappearance was found to follow (20):

$$r_T = K p_T p_H / (1 + K_T p_T + K_{\text{H}_2\text{S}} p_{\text{H}_2\text{S}})^2 \quad (2)$$

where  $r_T$  is the rate of disappearance of thiophene.  $p_T$ ,  $p_H$  and  $p_{\text{H}_2\text{S}}$  are the partial pressures exerted by thiophene, hydrogen and hydrogen sulphide in mm Hg respectively.  $K$  is the reaction rate constant, moles/(gram catalyst)(min)(mm Hg)<sup>2</sup>,  $K_T$  and  $K_{\text{H}_2\text{S}}$  are the adsorption equilibrium constants for thiophene and  $\text{H}_2\text{S}$  respectively, (mm Hg)<sup>-1</sup>. Both hydrogen sulphide and

thiophene were observed to inhibit the rate of thiophene disappearance significantly. Roberts (20) also established the following butene formation rate based on the assumption that all butene desorbs and re-adsorbs before it is hydrogenated to butane.

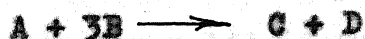
$$r_C = \hat{K} p_B / (1 + \hat{K}_B p_B + \hat{K}_{H_2S} p_{H_2S}) \quad (3)$$

where  $K$  is the reaction rate constant for second reaction, moles/(gram catalyst)(min), (mm Hg),  $\hat{K}_B$  and  $\hat{K}_{H_2S}$  are adsorption equilibrium constants for butene and  $H_2S$  respectively, (mm Hg)<sup>-1</sup> and  $p_B$  is the partial pressure of butene, mm Hg.

The second step in reaction scheme, that is, the hydrogenation of butene to butane, was also found to be retarded by the adsorption of hydrogen sulfide and butene, with butene exerting stronger effect. The fact that denominators of the two rate expressions, equation 2 and 3, are dissimilar suggests that the desulphurization of thiophene and hydrogenation of butene take place on different catalyst sites.

## B.2 Mathematical Formulation of the Problem:

For ease of expression we designate  $C_4H_4S$  as A,  $H_2$  as B,  $C_4H_8$  as C,  $H_2S$  as D and  $C_4H_{10}$  as E. Then the reaction becomes



(4)

and the rate expressions for the disappearance of thiophene (A) and the formation of butane (E) can be written as

$$-r_A = K P_A P_B / (1 + K_A P_A + K_D P_D)^2 \quad (5)$$

$$-r_E = \hat{K} P_C / (1 + \hat{K}_C P_C + \hat{K}_D P_D) \quad (6)$$

The rate expressions for other components can be obtained from simple stoichiometry

$$r_C = -r_A - r_E \quad (7a)$$

$$r_D = -r_A \quad (7b)$$

$$-r_B = -3 r_A + r_E \quad (7c)$$

#### Diffusion Inside the Pore:

At steady state, a mass balance of the component diffusing in and out from a small thin shell of thickness  $dz$  at a distance  $z$  from the pore mouth becomes

(Rate of diffusion in the direction of  $z$  at  $z = z$ ) (Rate of diffusion in the direction of  $z$  at  $z = z + dz$ ) = Rate of reaction in the shell.

$$-SD_A \left( \frac{dC_A}{dz} \right) - SD_A \left( -\frac{dC_A}{dz} - \frac{d^2 C_A}{dz^2} dz \right) = -S dz r_A \quad (8)$$

$$\text{or} \quad D_A \frac{d^2 C_A}{dz^2} = -r_A \quad (9)$$

where  $S$  is the cross sectional area of the pore,  $C_A$  is the concentration of component A and  $D_A$  is the diffusivity of component A. The above equation is valid if transport of material is only due to diffusion and bulk transport due to pressure gradient is



neglected. However, whenever there is change in number of moles/the pressure gradient will exist within the pore. Otani et.al.(19) have studied the effect of pressure gradient on the effect of pressure gradient on the effectiveness of porous catalysts and observed that for small capillaries where Knudsen diffusion predominates the influence is insignificant and for a typical bi-disperse catalyst pellet, they concluded that the effect can be important only if the change in moles exceeds two. In general

$$D_1 \frac{d^2 C_1}{dz^2} = -r_1 \quad (10)$$

where  $r_1$  is the rate of formation of component 1 and negative sign indicates the rate of disappearance. Using the values of  $r_A$ ,  $r_C$  and  $r_E$  from equation (10) in equation (7) and assuming ideal gas behaviour, the following partial pressure expressions are obtained after integration and substitution of limits

$$p_C = p_{C_0} + \frac{D_A}{D_C} (p_{A_0} - p_A) + \frac{D_E}{D_C} (p_{E_0} - p_E) \quad (11a)$$

$$p_B = p_{B_0} - \frac{3D_A}{D_B} (p_{A_0} - p_A) + \frac{D_E}{D_B} (p_{E_0} - p_E) \quad (11b)$$

$$p_D = p_{D_0} + \frac{D_A}{D_D} (p_{A_0} - p_A) \quad (11c)$$

When these values are substituted in the rate equations (5) and (6) the following expression results

$$\frac{D_A}{RT} \frac{d^2 p_A}{dz^2} = \frac{K p_A \left[ p_{B_0} - \frac{3D_A}{D_B} (p_{A_0} - p_A) + \frac{D_E}{D_B} (p_{E_0} - p_E) \right]}{\left[ 1 + K_A p_A + K_D \left\{ p_{D_0} + \frac{D_A}{D_D} (p_{A_0} - p_A) \right\} \right]^2} \quad (12)$$

$$-\frac{D_E}{RT} \frac{d^2 p_E}{dz^2} = \frac{\hat{K} \left[ p_{CO} + \frac{D_A}{D_C} (p_{Ao} - p_A) + \frac{D_E}{D_C} (p_{Eo} - p_E) \right]}{\left[ 1 + \hat{K}_C \left\{ \frac{D_A}{D_C} (p_{Ao} - p_A) + \frac{D_E}{D_C} (p_{Eo} - p_E) \right\} + \hat{K}_D \left\{ p_{Do} + \frac{D_A}{D_D} (p_{Ao} - p_A) \right\} \right]} \quad (13)$$

These equations can be changed into dimensionless form by defining

$$\phi = p/p_o \quad \eta = z/L \quad K_1 = K p_o^2$$

$$\frac{K}{K p_o} \equiv K_2 \text{ to give}$$

$$\frac{d^2 \phi_A}{d\eta^2} = + \frac{\phi_M^2 \phi_A \left[ \alpha + 3 \frac{D_A}{D_B} \phi_A - \frac{D_E}{D_B} \phi_E \right]}{(1 + K_A p_o) \left[ \frac{1}{1 + K_A p_o} + \frac{K_A p_o}{1 + K_A p_o} (\phi_A + \gamma - \frac{K_D}{K_A} \frac{D_A}{D_D} \phi_A) \right]^2} \quad (14)$$

where

$$\alpha = \frac{p_{Bo}}{p_o} - \frac{D_A}{D_B} \frac{p_{Ao}}{p_o} + \frac{D_E}{D_B} \frac{p_{Eo}}{p_o}$$

$$\gamma = \frac{K_D}{K_A} \frac{p_{Do}}{p_o} + \frac{K_D}{K_A} \frac{D_A}{D_D} \frac{p_{Ao}}{p_o}$$

$$\phi_M = L \sqrt{\frac{K_1 R T}{p_o D_A (1 + K_A p_o)}} \quad (15)$$

and

$$\frac{d^2 \phi_E}{d\eta^2} = \frac{-K_2 \phi_M^2 \left[ \xi - \frac{D_A}{D_C} \phi_A - \frac{D_E}{D_C} \phi_E \right]}{\left[ \frac{1}{1 + K_A p_o} + \frac{K_A p_o}{K_A (1 + K_A p_o)} \left\{ \xi - \frac{D_A}{D_C} \phi_A - \frac{D_E}{D_C} \phi_E \right\} + \frac{K_D K_A p_o}{K_A (1 + K_A p_o)} \left\{ \chi - \frac{D_A}{D_D} \phi_A \right\} \right]} \quad (16)$$

where

$$\begin{aligned}\xi &= \phi_{Co} + \frac{D_A}{D_C} \phi_{Ao} + \frac{D_E}{D_C} \phi_{Eo} \\ \chi &= \phi_{Do} + \frac{D_A}{D_D} \phi_{Ao}\end{aligned}\quad (17)$$

The equations 14 and 16 are to be solved with the following conditions

$$\begin{aligned}\phi_A (\text{at } \eta = 0) &= \phi_{Ao} \\ \phi_E (\text{at } \eta = 0) &= \phi_{Eo} \\ \frac{d\phi_A}{d\eta} (\text{at } \eta = 1) &= \frac{d\phi_E}{d\eta} (\text{at } \eta = 1) = 0\end{aligned}\quad (18)$$

The last boundary condition is obtained because no reaction, and hence no diffusion, can take place at the end of the pore. Recognizing that the overall reaction rate within the pore equals the rate of mass transfer across the pore mouth, the rate of reactions of A and E will be proportional to  $D_A \frac{d\phi_A}{d\eta} \Big|_{\eta=0}$  and

$$D_E \frac{d\phi_E}{d\eta} \Big|_{\eta=0} \text{ and, therefore selectivity with diffusion effects}$$

$$S_D = \frac{r_E}{-r_A} = \frac{-r_A - r_E}{-r_A} = \frac{\frac{d\phi_A}{d\eta} \Big|_{\eta=0} - \frac{D_E}{D_A} \frac{d\phi_E}{d\eta} \Big|_{\eta=0}}{\frac{d\phi_A}{d\eta} \Big|_{\eta=0}} \quad (19)$$

The selectivity value can, therefore, be obtained by knowing

$$\left. \frac{d\phi_A}{d\eta} \right|_{\eta=0} \quad \text{and} \quad \left. \frac{d\phi_E}{d\eta} \right|_{\eta=0}$$

The rates of reaction without diffusion effect can simply be written as

$$-r_A = K_1 \phi_A \phi_B / \left[ (1 + K_A p_o (\phi_A + \frac{K_D}{K_A} \phi_D))^2 \right] \quad (20)$$

$$-r_E = K_1 K_2 \phi_C / \left[ 1 + K_A p_o (\phi_C \frac{K_C}{K_A} + \phi_D \frac{K_D}{K_A}) \right] \quad (21)$$

Hence selectivity without diffusion effects

$$S_0 = 1 - \frac{\phi_C K_2 \left[ 1 + K_A p_o (\phi_A + \frac{K_D}{K_A} \phi_D) \right]^2}{\left[ 1 + K_A p_o (\phi_C \frac{K_C}{K_A} + \phi_D \frac{K_D}{K_A}) \right] \phi_A \phi_B} \quad (21)$$

### B-3: Product Distribution and Selectivity with Conversion:

The computation was carried out by taking the initial partial pressures of reactants A and B as 0.1 and 0.9 respectively and the selectivity calculated for any given value of modified Thiele parameter using this value of selectivity and taking a constant increment 0.001 (one percent of the initial partial pressure of A) change in the value of partial pressure of A the product distribution for next step was calculated.

If  $\Delta$  is the change in the partial pressure of A and  $S_{D_0}$  the selectivity, then the new values of the partial pressures



of B, C, D and E can be calculated from the following stoichiometric relations

$$\begin{aligned}
 A_1 &= A_0 - \Delta \\
 B_1 &= B_0 - (3 \times S_{D_0} + 4(1 - S_{D_0}))\Delta \\
 C_1 &= C_0 + S_{D_0} \times \Delta \\
 D_1 &= D_0 + \Delta \\
 E_1 &= E_0 + (1 - S_{D_0})\Delta
 \end{aligned}
 \tag{22}$$

Due to changes in the number of moles of the reactants and products, the partial pressure of each component was normalized by dividing the individual partial pressure by sum of the partial pressures of all components. These normalized values of partial pressures were then used to calculate the new value of selectivity,  $S_{D_1}$ . The values of partial pressures for next step were calculated from equation (22) by changing the numerical subscripts, that is, writing 2 in place of 1 and 1 in place of 0. The procedure was repeated upto any desired conversion. Computations were made for modified Thiele parameter values of 0.2, 0.5, 1.0, 1.5 and 2.0 and thiophene conversion of 0 to 100 percent.

For the study of selectivity without any diffusion limitation, the selectivity was found to be very sensitive to the changes in the partial pressure values. An iterative technique was, therefore, used to obtain the truly representative average value of selectivity for any incremental change in the

partial pressure of A. In the iteration procedure, selectivity  $S_0$  was computed for partial pressure values of  $A_0$ ,  $B_0$ ,  $C_0$ ,  $D_0$  and  $E_0$ . For incremental change  $\Delta$  as a first approximation the new values of  $A_{11}$ ,  $B_{11}$ ,  $C_{11}$ ,  $D_{11}$  and  $E_{11}$  were computed from equation (22) by replacing  $S_0$  in place of  $S_{D_0}$ . New selectivity value  $S_{11}$  was then computed from partial pressure values of  $A_{11}$  to  $E_{11}$ . The improved value of selectivity that is  $(S_0 + S_{11})/2$ , was taken and with this, new values of  $A_{12}$ ,  $B_{12}$ ,  $C_{12}$ ,  $D_{12}$  and  $E_{12}$  were computed from equation (22). New selectivity value was then computed from partial pressures  $A_{12}$  to  $E_{12}$ . This procedure was continued till the difference of  $(n-1)^{th}$  and  $n^{th}$  selectivity was less than 0.0001. This iterative technique was used to calculate the values of selectivity,  $S_0$ , for 0 to 100 percent conversion of thiophene.

#### B-4: Results and Discussions:

For any given system, only the modified Thiele parameter,  $\phi_M$  can be varied independently by varying catalyst pellet size. All other dimensionless variables involving diffusion, adsorption or reaction rate constant assume constant values. Robert(20) gave the following values for the constants at 250°C.

$$K(\text{moles/gram catalyst, min., mm Hg}^2) = 0.178 \times 10^{-8}$$

$$K_A(\text{mm Hg}^{-1}) = 0.0284$$

$$K_D(\text{mm Hg}^{-1}) = 0.0237$$

$$K(\text{moles/gram catalyst, min, mm Hg}) = 0.269 \times 10^{-5}$$

$$K_C(\text{mm Hg}^{-1}) = 0.463$$

$$K_D(\text{mm Hg}^{-1}) = 0.0884$$

where  $K$  is reaction rate constant,  $K_A$  and  $K_D$  are adsorption equilibrium constants for the first step of the reaction.  $K$  is the reaction rate constant,  $K_C$  and  $K_D$  are adsorption equilibrium constants for the second step of the reaction. A, B, C, D and E are representing thiophene, hydrogen, butene, hydrogen sulfide and butane respectively. These constants were changed to the following dimensionless variables and then used for the calculation of the selectivity.

$$K_1 \equiv K p_o^2$$

$$K_2 \equiv K_1 / K p_o$$

$$K_A p_o$$

Ratio of diffusivities,  $D_B/D_A$ ,  $D_C/D_A$ ,  $D_D/D_A$  and  $D_E/D_A$

Ratio of adsorption equilibrium constants  $K_D/K_A$ ,

$$K_C/K_A, K_D/K_A$$

The values of effective diffusivities of components B, C, D and E were calculated using the method as described by Robert(20) while calculating the effective diffusivity of thiophene. The values of binary diffusion coefficients (for diffusion in hydrogen) and Knudsen diffusion coefficient were calculated using the relationships given by Sherwood and Satterfield (2). The results presented in Tables 9 to 14 show the percent thiophene converted, normalized values of partial pressures of component A, B, C, D and E, ratio of C to E, percent conversion to C, for different values of modified Thiele parameter in the range of 0.2 to 2.0 as well as for a case when no diffusion limitation exists.

The value of selectivity when diffusion limitations does not exist as given in Table 9 page 54 indicate that these are very sensitive to the composition and decreases rapidly as conversion of thiophene to butene or butane increases. The selectivity value changes from unity at zero percent thiophene conversion to a minimum value nearly -1.145 at conversion level of approximately 92 percent. As the conversion level increases further the selectivity value also increases and attains a value of approximately - 0.477 at 100 percent conversion. Percent conversion to butene increases with increase in thiophene conversion upto a conversion level of 64 percent and then it is found to decrease with further increase in conversion of thiophene. The maximum butene conversion is found to be 23.74 percent at a thiophene conversion of 60 percent. The ratio of butene to butane in product decreases from infinity to zero as the thiophene conversion increases from zero to 100 percent. These observations are in conformity with those obtained for simple series reaction(23)

The following are some of the observations made on analysing the results presented in tables 10 to 14 and figure 2 with diffusion limitations:

(i) The values of selectivity when diffusion limitations exist were less at higher values of modified Thiele parameter than at lower values of Thiele parameter. Thus the partial pressure of butene was less at higher values of Thiele parameter than at lower values of Thiele parameter.

(11) The ratio of butene to butane in product decreased with the increase in conversion at lower values of modified Thiele parameter i.e. at 0.2 and 0.5, but was almost constant at higher values of modified Thiele parameter, i.e. at 1.5 and 2. In this study, with diffusion limitations, the ratio of butene to butane in product attains a constant value of 0.53 at 100 percent conversion of thiophene. These observations were not in conformity with the results obtained when no diffusion limitations exist. The expected behaviour of the results in Fig. 2 and tables 10 to 14 with diffusion limitations is that, they should be always below the result for without diffusion limitation. The reason for this doubtful behaviour may be the approximate results obtained with invariant imbedding technique. This approximation of the results will be multiplied as the thiophene conversion will proceed to 100 percent with  $\Delta$  increment for each step of conversion and hence this may be the reason of 34 percent of butene at 100 percent thiophene conversion.

TABLE 9: DATA FOR PRODUCT DISTRIBUTION AND SELECTIVITY FOR NO DIFFUSION LIMITATION

% A converted	A	B	C	D	E	Ratio C/E	% converted to C	S <sub>D</sub>
0.0	0.1	0.9	0.0	0.0	0.0	-	0.0	1.0
4.98	0.096	0.894	0.004	0.005	0.001	3.99	3.98	0.7
9.90	0.092	0.888	0.007	0.010	0.003	2.51	7.08	0.595
15.73	0.088	0.880	0.011	0.016	0.006	1.91	10.32	0.531
20.52	0.084	0.873	0.013	0.022	0.008	1.64	12.74	0.488
25.25	0.080	0.867	0.016	0.027	0.010	1.45	14.94	0.448
29.92	0.076	0.860	0.018	0.032	0.014	1.30	16.90	0.407
35.45	0.071	0.852	0.021	0.039	0.018	1.15	18.99	0.354
39.99	0.067	0.845	0.023	0.044	0.022	1.05	20.47	0.306
45.36	0.062	0.836	0.025	0.051	0.027	0.935	21.98	0.242
50.63	0.057	0.827	0.026	0.058	0.032	0.831	22.97	0.169
54.97	0.052	0.819	0.027	0.064	0.037	0.748	23.53	0.098
60.08	0.047	0.810	0.028	0.071	0.043	0.654	23.74	0.0006
65.10	0.042	0.800	0.028	0.079	0.050	0.562	23.42	-0.116
70.03	0.037	0.791	0.028	0.086	0.059	0.472	22.46	-0.256
75.66	0.031	0.779	0.026	0.095	0.070	0.369	20.39	-0.456
80.38	0.025	0.768	0.023	0.104	0.081	0.282	17.68	-0.664
85.00	0.020	0.756	0.018	0.112	0.094	0.197	13.99	-0.900
90.25	0.013	0.742	0.012	0.122	0.111	0.104	8.53	-1.127
95.35	0.007	0.728	0.004	0.133	0.129	0.032	2.98	-0.960
99.61	0.001	0.715	0.000	0.142	0.142	0.002	0.195	-0.477



TABLE 10: DATA FOR PRODUCT DISTRIBUTION AND SELECTIVITY FOR  $\phi_M = 0.2$ 

% A converted	A	B	C	D	E	Ratio C/E	% converted to C	S <sub>D</sub>
0.0	0.1	0.9	0.0	0.0	0.0	-	0.0	0.754
4.98	0.096	0.894	0.004	0.005	0.002	2.31	3.47	0.639
9.90	0.092	0.887	0.007	0.010	0.004	1.92	6.50	0.585
14.76	0.088	0.881	0.010	0.015	0.006	1.69	9.27	0.549
20.50	0.084	0.873	0.013	0.022	0.009	1.52	12.36	0.516
25.24	0.080	0.867	0.016	0.027	0.011	1.41	14.75	0.491
29.91	0.076	0.859	0.018	0.032	0.014	1.32	17.00	0.467
35.44	0.071	0.852	0.021	0.039	0.017	1.23	19.52	0.439
39.99	0.067	0.845	0.024	0.044	0.021	1.16	21.47	0.414
45.36	0.062	0.836	0.027	0.051	0.024	1.09	23.63	0.384
50.65	0.056	0.828	0.029	0.058	0.029	1.02	25.58	0.350
55.86	0.051	0.819	0.032	0.065	0.033	0.958	27.33	0.314
60.13	0.057	0.811	0.034	0.071	0.037	0.910	28.62	0.282
65.18	0.042	0.802	0.036	0.078	0.042	0.850	29.96	0.240
70.16	0.036	0.793	0.038	0.085	0.048	0.795	31.06	0.197
75.05	0.031	0.783	0.040	0.093	0.053	0.740	31.94	0.153
80.65	0.024	0.772	0.041	0.102	0.061	0.681	32.67	0.106
85.36	0.019	0.761	0.043	0.110	0.067	0.634	33.15	0.080
89.99	0.013	0.751	0.044	0.118	0.074	0.592	33.47	0.079
95.28	0.006	0.739	0.045	0.127	0.082	0.554	33.96	0.116
99.74	0.000	0.728	0.047	0.136	0.089	0.530	34.55	0.104

TABLE 11: DATA FOR PRODUCT DISTRIBUTION AND SELECTIVITY FOR  $\phi_M = 0.5$ 

% A converted	A	B	C	D	E	Ratio C/E	% converted to C	S <sub>D</sub>
0.0	0.1	0.9	0.0	0.0	0.0	-	0.0	0.557
4.98	0.096	0.894	0.003	0.005	0.002	1.2	2.71	0.530
9.89	0.092	0.887	0.006	0.010	0.005	1.14	5.27	0.509
15.71	0.088	0.880	0.009	0.016	0.008	1.09	8.18	0.487
20.49	0.084	0.873	0.011	0.022	0.011	1.05	10.47	0.470
25.00	0.080	0.866	0.014	0.027	0.013	1.01	12.16	0.452
30.80	0.075	0.858	0.016	0.033	0.017	0.976	15.13	0.431
35.39	0.071	0.851	0.019	0.039	0.020	0.933	17.08	0.413
40.82	0.066	0.843	0.021	0.046	0.024	0.895	19.27	0.391
45.28	0.062	0.836	0.023	0.051	0.027	0.864	20.98	0.381
50.55	0.057	0.827	0.026	0.058	0.032	0.827	22.89	0.347
55.75	0.052	0.818	0.029	0.065	0.036	0.792	24.64	0.321
60.00	0.047	0.811	0.031	0.071	0.040	0.763	25.97	0.299
65.05	0.042	0.802	0.033	0.078	0.045	0.729	27.42	0.272
70.01	0.037	0.792	0.035	0.086	0.050	0.695	28.71	0.245
75.03	0.030	0.782	0.037	0.094	0.057	0.658	30.03	0.215
80.48	0.025	0.771	0.039	0.102	0.063	0.627	31.01	0.194
85.18	0.019	0.761	0.041	0.110	0.069	0.598	31.89	0.179
90.57	0.012	0.750	0.043	0.119	0.076	0.569	32.84	0.174
95.10	0.007	0.739	0.045	0.127	0.082	0.547	33.64	0.184
99.56	0.001	0.729	0.047	0.135	0.088	0.530	34.50	0.204



TABLE 19: DATA FOR PRODUCT DISTRIBUTION AND SELECTIVITY FOR  $\phi_M = 1.0$ 

% A converted	A	B	C	D	E	Ratio C/E	% converted to C	S <sub>D</sub>
0.0	0.1	0.9	0.0	0.0	0.0	-	0.0	0.400
4.97	0.096	0.894	0.002	0.005	0.003	0.663	1.98	0.396
9.88	0.092	0.887	0.004	0.010	0.006	0.656	3.92	0.391
15.69	0.088	0.879	0.006	0.016	0.010	0.649	6.18	0.386
20.46	0.084	0.873	0.009	0.022	0.013	0.643	8.00	0.381
25.17	0.080	0.866	0.011	0.027	0.017	0.636	9.79	0.376
30.74	0.075	0.858	0.013	0.033	0.021	0.629	11.87	0.369
35.31	0.071	0.851	0.015	0.039	0.024	0.622	13.54	0.364
40.70	0.066	0.842	0.017	0.046	0.028	0.614	15.50	0.357
45.17	0.062	0.835	0.019	0.051	0.032	0.608	17.08	0.352
50.42	0.057	0.827	0.022	0.058	0.036	0.600	18.90	0.345
55.59	0.052	0.818	0.024	0.065	0.041	0.592	20.68	0.339
60.68	0.047	0.809	0.027	0.072	0.046	0.585	22.39	0.332
65.69	0.042	0.800	0.029	0.079	0.050	0.578	24.05	0.326
70.62	0.036	0.790	0.032	0.087	0.055	0.570	25.64	0.320
75.47	0.031	0.781	0.034	0.094	0.060	0.563	27.18	0.314
80.24	0.025	0.771	0.036	0.102	0.065	0.556	28.67	0.309
85.71	0.019	0.760	0.039	0.111	0.072	0.548	30.34	0.303
90.32	0.013	0.750	0.042	0.119	0.077	0.542	31.73	0.298
95.60	0.006	0.738	0.045	0.128	0.083	0.534	33.30	0.294
99.30	0.001	0.729	0.047	0.135	0.088	0.530	34.39	0.294

TABLE 13: DATA FOR PRODUCT DISTRIBUTION AND SELECTIVITY AT  $\phi_M = 1.5$ 

% A converted	A	B	C	D	E	Ratio C/E	% converted to C	S <sub>D</sub>
0.0	0.1	0.9	0.0	0.0	0.0	-	0.0	0.325
4.97	0.096	0.894	0.002	0.005	0.003	0.488	1.63	0.332
9.88	0.093	0.887	0.003	0.010	0.007	0.495	3.27	0.337
15.68	0.088	0.879	0.006	0.016	0.011	0.502	5.24	0.343
20.45	0.084	0.873	0.007	0.022	0.014	0.507	6.88	0.347
25.15	0.080	0.866	0.009	0.027	0.018	0.513	8.52	0.350
30.71	0.095	0.858	0.011	0.033	0.022	0.518	10.48	0.353
35.28	0.071	0.851	0.013	0.039	0.026	0.522	12.10	0.355
40.68	0.067	0.842	0.016	0.046	0.030	0.526	14.02	0.356
45.12	0.062	0.835	0.018	0.051	0.034	0.528	15.60	0.357
50.36	0.057	0.826	0.020	0.058	0.038	0.531	17.47	0.356
55.53	0.052	0.818	0.023	0.065	0.043	0.533	19.31	0.355
60.61	0.047	0.809	0.025	0.072	0.047	0.535	21.10	0.354
65.61	0.042	0.800	0.028	0.079	0.052	0.535	22.88	0.351
70.54	0.036	0.790	0.030	0.087	0.057	0.536	24.60	0.349
75.38	0.031	0.781	0.033	0.094	0.061	0.535	26.28	0.346
80.15	0.025	0.771	0.036	0.102	0.066	0.535	27.92	0.342
85.62	0.019	0.760	0.039	0.111	0.072	0.534	29.50	0.339
90.23	0.013	0.750	0.041	0.119	0.077	0.532	31.34	0.336
95.51	0.006	0.738	0.044	0.128	0.084	0.531	33.10	0.332
99.96	0.000	0.728	0.047	0.136	0.089	0.529	34.57	0.323

TABLE 14: DATA FOR PRODUCT DISTRIBUTION AND SELECTIVITY AT  $\phi_M = 2.0$ 

% A converted	A	B	C	D	E	Ratio C/E	% converted to C	S <sub>D</sub>
0.0	0.1	0.9	0.0	0.0	0.0	-	0.0	0.325
4.97	0.096	0.894	0.002	0.005	0.003	0.483	1.62	0.326
9.88	0.093	0.887	0.003	0.010	0.007	0.483	3.22	0.326
15.68	0.088	0.879	0.005	0.016	0.011	0.484	5.10	0.327
20.45	0.084	0.873	0.007	0.022	0.015	0.484	6.67	0.327
25.15	0.080	0.866	0.009	0.027	0.018	0.485	8.21	0.329
30.71	0.076	0.858	0.011	0.033	0.023	0.486	10.04	0.332
35.27	0.072	0.851	0.013	0.039	0.026	0.488	11.56	0.335
40.67	0.067	0.842	0.015	0.046	0.031	0.490	13.38	0.340
45.10	0.062	0.835	0.017	0.051	0.034	0.493	14.90	0.345
50.35	0.058	0.826	0.019	0.058	0.039	0.498	16.72	0.353
55.50	0.052	0.818	0.022	0.065	0.043	0.503	18.56	0.360
60.59	0.047	0.809	0.024	0.072	0.048	0.508	20.41	0.367
65.59	0.042	0.799	0.027	0.079	0.053	0.514	22.26	0.373
70.51	0.036	0.790	0.030	0.087	0.057	0.519	24.10	0.376
75.35	0.031	0.781	0.032	0.094	0.062	0.524	25.92	0.375
80.12	0.025	0.771	0.035	0.102	0.067	0.528	27.70	0.370
85.59	0.019	0.760	0.038	0.111	0.072	0.531	29.69	0.358
90.19	0.013	0.750	0.041	0.119	0.077	0.532	31.32	0.344
95.48	0.006	0.738	0.044	0.128	0.084	0.531	33.10	0.330
99.93	0.000	0.728	0.047	0.136	0.089	0.529	34.56	0.344



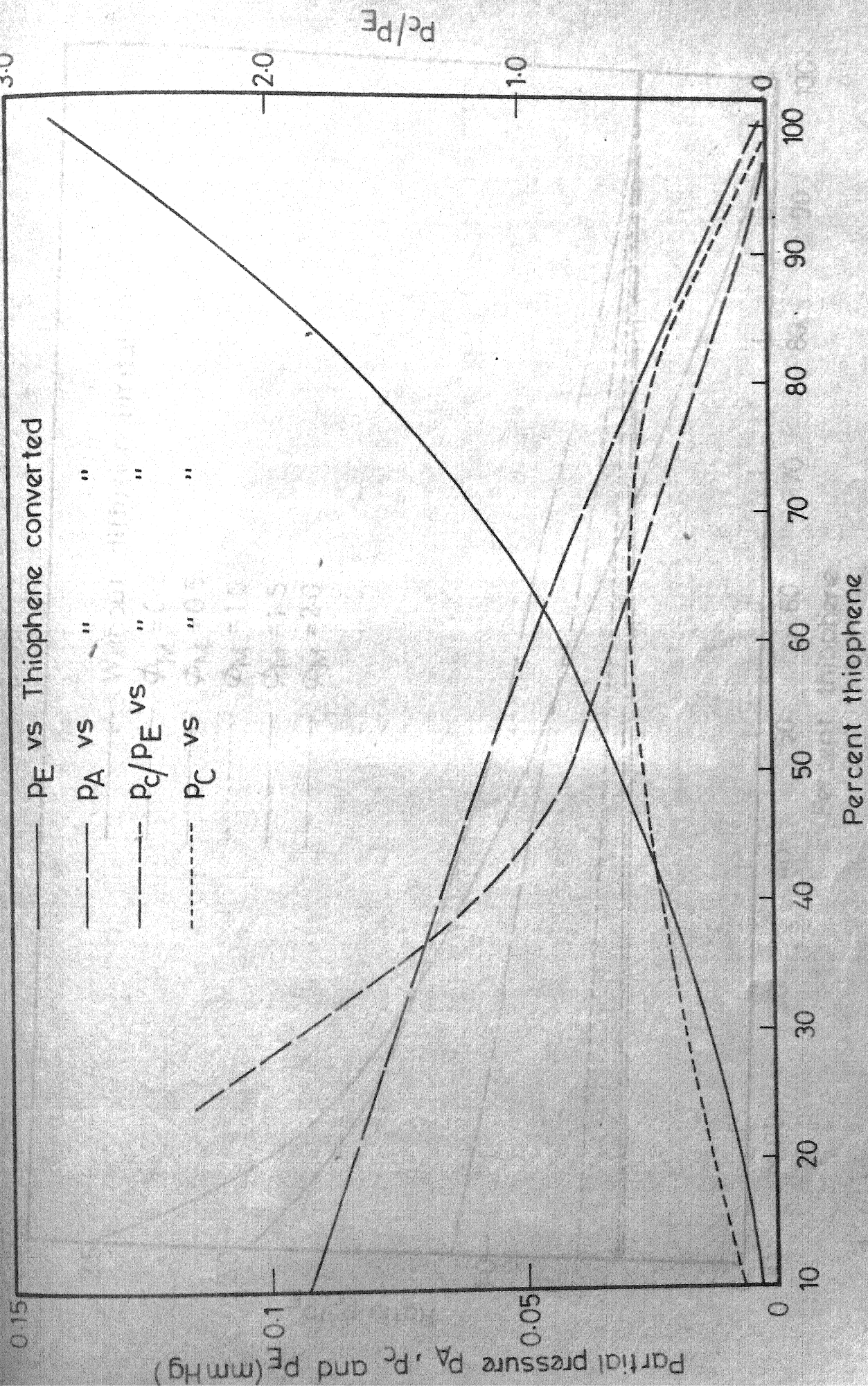


Fig. 1 - Partial pressure of thiophene,  $P_A$ , Butane,  $P_C$ , Butane,  $P_E$  and ratio of Butane to Butane,  $P_C/P_E$  as a function of percent Thiophene converted.

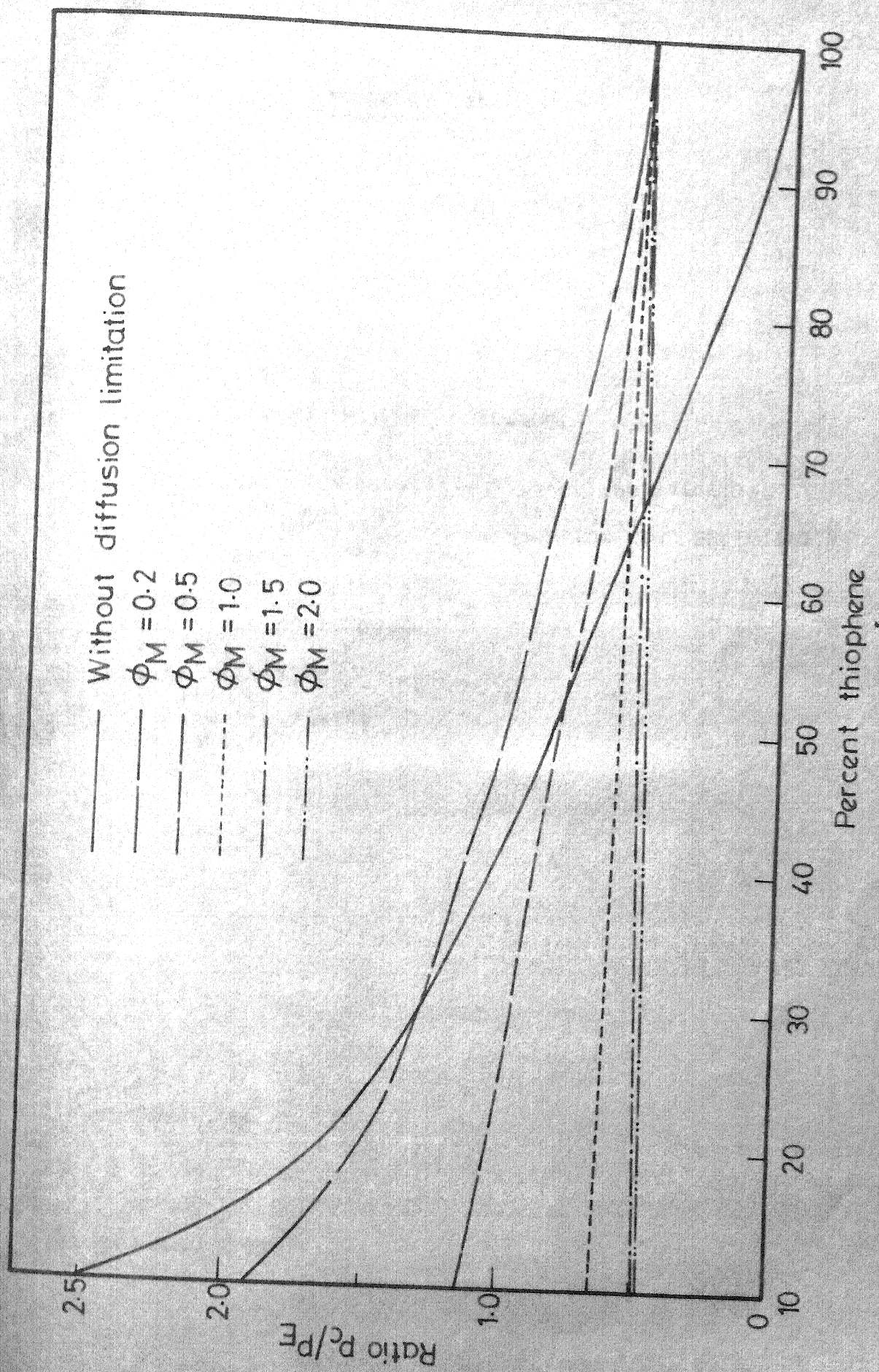


Fig. 2—Ratio of butene to butane,  $P_C/P_E$ , as a function of percent thiophene converted for selected values of modified Thiele parameter,  $\phi_M$ , and without diffusion limitation.



# APPENDIX B5

CGG094,TIME030,FAGES035,NAME J.C.GUPTA

B  
C

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DIMENSION U(4,4),V(4,4),W(4,4),X(3),AA(2),BB(2),CC(2)
GENERAL PROGRAMME FOR SERIES REACTIONS
FOR EFFECT OF DIFFUSION AND ADSORPTION ON SELECTIVITY
RATIO USING COMPLEX REACTIONS
READ 61,((U(K,L),L=1,3),K=1,3)
FORMAT(3F15.8)
EQUIVALENCE (CC,AML),(DO,EML)
COMMON A,B(20)
READ51,A,(B(I),I=1,10)
FORMAT(11F7.4)
PRINT 69,A,(B(I),I=1,10)
FORMAT(10X,11F9.4)
VV=1.
PP=.1
QQ=.9
GG=0.
HH=0.
WW=0.
DEL=.001
E1ML=0.0
EOML=0.
EML=0.
C1ML=-.001
CML=-.001
COML=-.001
D1ML=-.001
DML=-.001
DOML=-.001
AML=.101
A1ML=.101
AOML=.101
B1ML=.903
BOML=.903
BML=.903
MM=0
UU=1.
DO 100 IK=1,120

```

```

A1ML=A1ML-DEL
C1ML=C1ML+DEL*VV
D1ML=D1ML+DEL
E1ML=E1ML+DEL*(1.-VV)
B1ML=B1ML-(3.*VV+4.*(1.-VV))*DEL
AOML=AOML-DEL
COML=COML+DEL*UU
DOML=DOML+DEL
EOML=EOML+(1.-UU)*DEL
BOML=BOML-(3.*UU+4.*(1.-UU))*DEL
AML=AML-DEL
CML=CML+DEL*VV
DML=DML+DEL
EML=EML+(1.-VV)*DEL
BML=BML-(3.*VV+4.*(1.-VV))*DEL
IF(EML)501,500,501
GML=0.
GO TO 505
GML=CML/EML
M=0
IF(EOML)511,521,511
GOML=0.
GO TO 506
GOML=COML/EOML
M=0
SIGMA=AML+BML+CML+DML+EML
AML=AML/SIGMA
BML=BML/SIGMA
CML=CML/SIGMA
DML=DML/SIGMA
EML=EML/SIGMA
APCN=(1.-AML/(AML+CML+EML))*100.
CPCN=(CML/(AML+CML+EML))*100.
PRINT 333,AML,BML,CML,DML,EML,GML,APCN,CPCN
3 FORMAT(10X,8F12.6)
WSIGMA=AOML+BOML+COML+DOML+EOML
AOML=AOML/WSIGMA
BOML=BOML/WSIGMA
COML=COML/WSIGMA
DOML=DOML/WSIGMA
EOML=EOML/WSIGMA
5 PRINT 555,AOML,BOML,COML,DOML,EOML,GOML
5 FORMAT(6F12.6)
DO 99 J=8,10
N=0
N1=0
N2=0
N3=0
N4=0
N5=0
R=J
Q=1./R
P=Q*Q
C=C0
D=D0

```

```

5  N=N+1
   C1=C-P*F(C,D)
   D1=D-P*G(C,D)
   C2=C1-P*F(C1,D1)
   D2=D1-P*G(C1,D1)
   C1=C2-P*F(C2,D2)
   D1=D2-P*G(C2,D2)
   GO TO(7,28,7,29,7,1,7,12,7,3,7,3,7,1,7,14,7,6,7,6,7,1,7,6,7,3,7,3,
1  7,1,7,21,7,8,7,8,7,1,7,8,7,3,7,3,7,1,7,8,7,6,7,6,7,1,7,6,7,3,7,3,
2  7,1,7,19,7,4,7,4,7,1,7,4,7,3,7,3,7,1,7,4,7,6,7,6,7,1,7,6,7,3,7,3,
3  7,1,7,4,7,8,7,8,7,1,7,8,7,3,7,3,7,1,7,8,7,6,7,6,7,1,7,6,7,3,7,3,
4  7,1,7,25),N
7  C3=C-P*(F(C,D)+F(C1,D1)+F(C2,D2))
   D3=D-P*(G(C,D)+G(C1,D1)+G(C2,D2))
   C=C3
   D=D3
   GO TO 5
28 C=C0
   D=D0
11 C4=C-P*(F(C,D)+F(C1,D1)+F(C2,D2)+F(C3,D3))
   D4=D-P*(G(C,D)+G(C1,D1)+G(C2,D2)+G(C3,D3))
   C=C4
   D=D4
   GO TO 5
29 C=C0
   D=D0
15 C5=C-P*(F(C,D)+F(C1,D1)+F(C2,D2)+F(C3,D3)+F(C4,D4))
   D5=D-P*(G(C,D)+G(C1,D1)+G(C2,D2)+G(C3,D3)+G(C4,D4))
1  C=C5
   D=D5
   N1=N1+1
   GO TO(5,11,5,11,5,11,5,11,5,11,5,11,5,11,5,11,
1  5,11,5,11,5,11,5,11,5,11,5,11,5,11,5,11),N1
12 C=C0
   D=D0
20 C6=C-P*(F(C,D)+F(C1,D1)+F(C2,D2)+F(C3,D3)+F(C4,D4)+F(C5,D5))
   D6=D-P*(G(C,D)+G(C1,D1)+G(C2,D2)+G(C3,D3)+G(C4,D4)+G(C5,D5))
3  C=C6
   D=D6
   N2=N2+1
   GO TO(5,11,15,5,11,15,5,11,15,5,11,15,
1  5,11,15,5,11,15,5,11,15,5,11,15),N2
14 C=C0
   D=D0
18 C7=C-P*(F(C,D)+F(C1,D1)+F(C2,D2)+F(C3,D3)+F(C4,D4)+F(C5,D5)+
1  F(C6,D6))
   D7=D-P*(G(C,D)+G(C1,D1)+G(C2,D2)+G(C3,D3)+G(C4,D4)+G(C5,D5)+
1  G(C6,D6))
6  C=C7
   D=D7
   N3=N3+1
   GO TO(5,11,15,20,5,11,15,20,5,11,15,20,5,11,15,20),N3

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```

21 C=C0
   D=D0
22 C8=C-P*(F(C,D)+F(C1,D1)+F(C2,D2)+F(C3,D3)+F(C4,D4)+F(C5,D5)+
1 F(C6,D6)+F(C7,D7))
   D8=D-P*(G(C,D)+G(C1,D1)+G(C2,D2)+G(C3,D3)+G(C4,D4)+G(C5,D5)+
1 G(C6,D6)+G(C7,D7))
   IF(J-8)8,40,8
40 V(1,4)=(C8-C0)/Q
   W(1,4)=(D8-D0)/Q
   GO TO 99
   C=C8
   D=D8
   N4=N4+1
   GO TO(5,11,15,20,18,5,11,15,20,18),N4
9 C=C0
   D=D0
   C9=C-P*(F(C,D)+F(C1,D1)+F(C2,D2)+F(C3,D3)+F(C4,D4)+F(C5,D5)+
1 F(C6,D6)+F(C7,D7)+F(C8,D8))
   D9=D-P*(G(C,D)+G(C1,D1)+G(C2,D2)+G(C3,D3)+G(C4,D4)+G(C5,D5)+
1 G(C6,D6)+G(C7,D7)+G(C8,D8))
   IF(J-9)4,41,4
41 V(2,4)=(C9-C0)/Q
   W(2,4)=(D9-D0)/Q
   GO TO 99
   C=C9
   D=D9
   N5=N5+1
   GO TO(5,11,15,20,18,22),N5
   C10=C0-P*(F(C0,D0)+F(C1,D1)+F(C2,D2)+F(C3,D3)+F(C4,D4)+F(C5,D5)+
1 F(C6,D6)+F(C7,D7)+F(C8,D8)+F(C9,D9))
   D10=D0-P*(G(C0,D0)+G(C1,D1)+G(C2,D2)+G(C3,D3)+G(C4,D4)+G(C5,D5)+
1 G(C6,D6)+G(C7,D7)+G(C8,D8)+G(C9,D9))
   V(3,4)=(C10-C0)/Q
   W(3,4)=(D10-D0)/Q
9 CONTINUE
8 DO 62 K=1,3
   DO 62 L=1,3
2 V(K,L)=U(K,L)
   DO 63 I=1,2
   II=I+1
   DO 63 K=II,3
   DO 63 L=II,4
3 V(K,L)=V(K,L)-V(I,L)*V(K,I)/V(I,I)
   DO 64 LQ=3,4
   LL=6-LQ
   LJ=LL-1
   DO 64 K=1,LJ
64 V(K,4)=V(K,4)-V(LL,4)*V(K,LL)/V(LL,LL)
   DO 65 K=1,3
65 X(K)=V(K,4)/V(K,K)
   DO 67 K=1,3
67 V(K,4)=W(K,4)
   M=M+1
   AA(M)=X(1)
   BB(M)=X(2)
   CC(M)=X(3)
   IF(M-2)68,98,98

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```

98  UU=1.-(B(1)*B(2)*COML*(1.+B(3)*(AOML+B(8)*DOML))**2)
    1/((1.+B(3)*(COML*B(9)+DOML*B(10)))*B(1)*AOML*BOML)
    VV=1.+B(7)*AA(2)/AA(1)
    AB=VV/UU
    PRINT 71,AA(1),AA(2),BB(1),CC(1),BB(2),CC(2) ,VV,UU,AB
71  FORMAT(9F12.6)
    IF(B1ML)222,444,444
222  GO TO 2
444  CONTINUE
    PRINT 130
130  FORMAT(/2X,120(1H-))
100  CONTINUE
    GO TO 2
97  STOP
    END
$IBFTC FUN1
    FUNCTION F(C,D)
    COMMON A,B(20)
    WW=0.
    HH=0.
    PP=.1
    QQ=.9
    GG=0.
    BB113=1./(1.+B(3))
    BB313=B(3)*BB113
    GAMA=B(8)*(HH+PP/B(6))
    ALPHA=QQ-3.*PP/B(4)+B(7)*WW/B(4)
    R=(A*A*C*(ALPHA+3.*C/B(4)-D*B(7)/B(4)))
    S=(1.+B(3))*(BB113+BB313*(C+GAMA-B(8)*C/B(6)))**2
    F=R/S
    RETURN
    END
$IBFTC FUN2
    FUNCTION G(C,D)
    COMMON A,B(20)
    WW=0.
    HH=0.
    PP=.1
    QQ=.9
    GG=0.
    BB113=1./(1.+B(3))
    BB313=B(3)*BB113
    ZEE=GG+PP/B(5)+B(7)*WW/B(5)
    SIE=HH+PP/B(6)
    SS= (BB113+BB313*B(9))*(ZEE-C/B(5)-B(7)*D/B(5))+BB313*B(10)
    R1=-A*A*B(2)*(ZEE-C/B(5)-D*B(7)/B(5))
    I*(SIE-C/B(6))
    G=R1/SS
    RETURN
    END
$ENTRY
1. .125 .015625
1. .11111111 .01234568
1. .1 .01

```